Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Hydrogen-Bonding Promoted Tunable Approach for the Access to Aza-bicyclo-[3.3.0]octanes and Cyclopenta[b] Pyrroles

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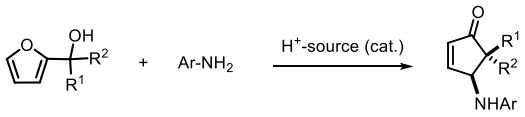
1. General Experimental

Unless otherwise mentioned in the experimental procedures, all the new reactions reported in the manuscript were performed using oven-dried or flame-dried glassware under argon/nitrogen atmosphere and stirred on a magnetic stirrer. Solvents received from commercial sources were used as received or dried using standard protocols before using in this study; freshly distilled THF was used in the study. Unless noted, all the reagents and catalysts were used as it was received from commercial sources and no further purification was made on those. TLC was performed using Merck silica gel 60 F 254 plates and used for reaction monitoring. TLC plates were visualized either under standard conditions; UV light (254 nm) or by using 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Silica gel of 230-400 mesh size was used for the flash column chromatography. The ^{1}H, ^{13}C NMR spectra were recorded on Avance III, Bruker at 400 MHz, 100 MHz and 376 MHz spectrometers respectively using $CDCl_3$. In the experimental section, the ^{1}H NMR chemicals shift are expressed in the form of ppm (δ) relative to δ = 7.26 for $CDCl_3$ whereas ^{13}C NMR chemical shift are expressed relative to δ = 77.16. The following abbreviations were used to refer to multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS.

2. Preparation of the starting material

*2.1. Preparation of 4-aminocyclopentenones: Following 4-aminocyclopentenone derivatives(**1a-1k**),*[1] ***(1l-1n)***[2] *were used in the study and prepared following the literature procedures.*



General Procedure: In a solution of furylcarbinol (1.0 equiv) and aniline (1.0 equiv) in CH_3CN (0.2 M to 0.05 M) was added catalytic acid (phosphomolybdic acid: 1.5 mol% or pTsOH: 10 mol%). The reaction mixture was placed in an oil bath (pre-heated at 85 ^oC) and progress was monitored via TLC. Upon completion of the reaction (ca. 2-3 h), water was added to the mixture and extraction was performed in ethyl acetate (3 × 100 mL). Combined organic layer was collected, washed with Brine (50 ml x 1), dried over anhydrous Na_2SO_4, filtered and concentrated in reduced pressure. The crude residue was purified by silica gel column chromatography to afford the 4-aminocyclopentenones.

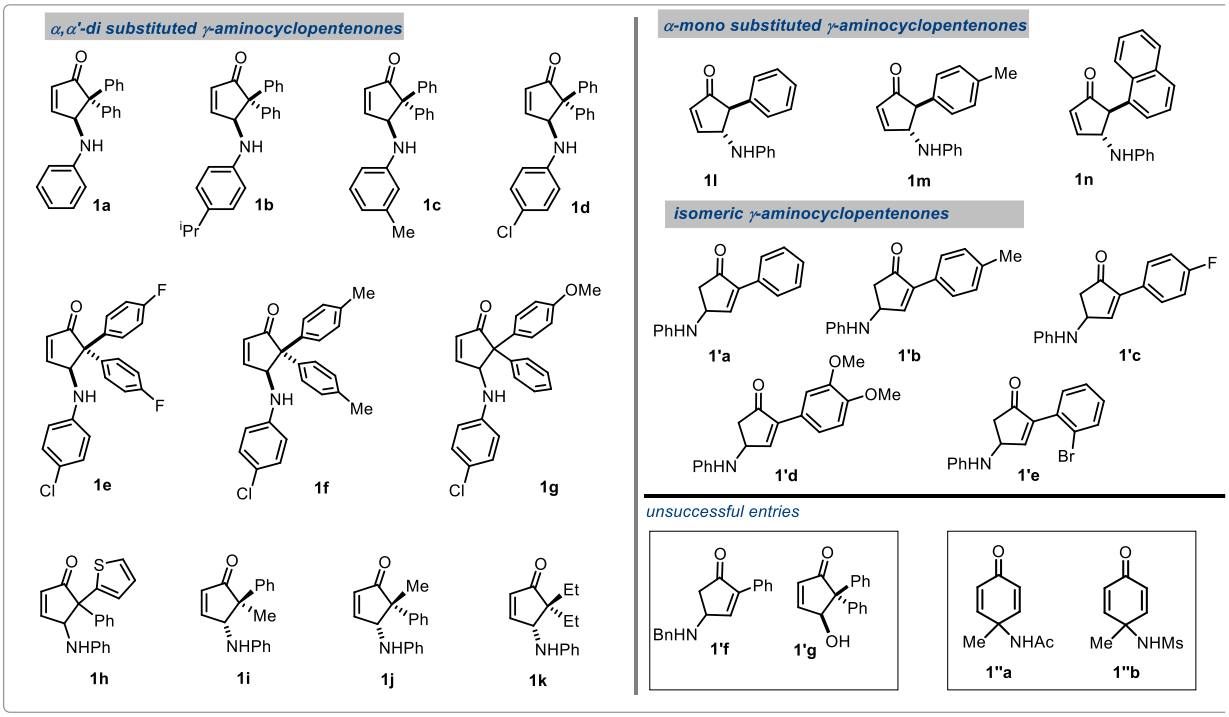
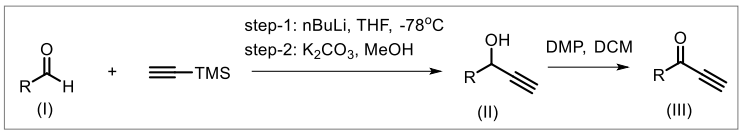


Figure S1: List of γ-aminocyclopentenones and other related structures used in the study

2.2. Preparation of alkyne derivative:

Alkyne derivative **2a** and **2b** are commercially available. Compounds **2c-2i**[3] and **2j**[4] were prepared following the literature procedure.



BuLi (1.05 equiv. 1.6 M in Hexane) solution was added dropwise to a precooled (-78°C) solution of TMS-acetylene (1.1 equiv.) in dry THF. After stirring for 1h, a solution of aldehyde (I) in THF was added to this mixture. After further stirring for 0.5-1.0 h, the reaction mixture was slowly warmed up to room temperature and quenched with water, and diluted with diethyl ether. The organic layer was collected, washed with brine, dried over anhy. Na_2SO_4 filtered and concentrated in reduced pressure. The crude was then dissolved in MeOH and was treated with K_2CO_3 (4.0 equiv) at room temperature. After consumption of the starting material (ca. 2h), the solvent was evaporated under reduced pressure. The crude was purified via silica gel column chromatography to obtain the propargyl alcohol (typical yields: 60-80%). Propargyl alcohol was then dissolved in dry DCM and was treated with Dess-Martin oxidant (1.1 equiv) at 0°C. After completion of the reaction (TLC monitored), the reaction mixture was passed through a short pad of celite, and the filtrate was with brine and sodium bicarbonate solution. The organic layer was dried over Na_2SO_4 and concentrated. The crude was purified by silica gel column chromatography to obtain alkynones (III).

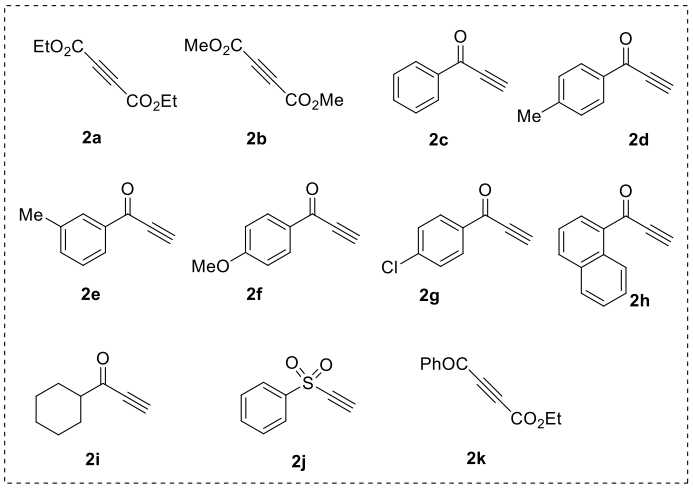
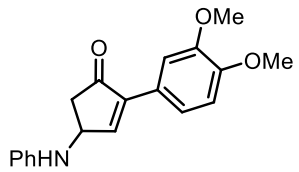


Figure S2: List of the alkyne used in the study

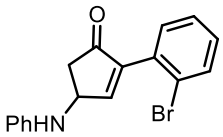
3. Characterization of newly synthesized γ-aminocyclopentenones

2-(3,4-Dimethoxyphenyl)-4-(phenylamino)cyclopent-2-en-1-one (1'd)



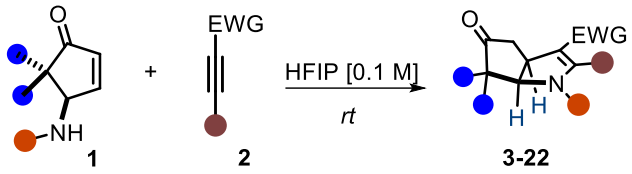
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.4 Hz, 1H), 7.40 - 7.36 (m, 2H), 7.28 - 7.24 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.77 - 4.75 (m, 1H), 3.92 (d, *J* = 5.7 Hz, 6H), 3.12 (dd, *J* = 18.6, 6.3 Hz, 1H), 2.44 (dd, *J* = 18.6, 2.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.0, 154.1, 149.9, 148.9, 146.6, 143.4, 129.6, 123.5, 120.4, 118.7, 113.7, 111.1, 110.4, 56.0(2), 51.0, 44.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{19}NNaO_3$calcd. 332.1263, found, 332.1255.

2-(2-Bromophenyl)-4-(phenylamino)cyclopent-2-en-1-one (1'e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.26 - 7.09 (m, 5H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.75 - 4.73 (m, 1H), 3.83 (s, 1H), 3.00 (dd, *J* = 18.6, 6.3 Hz, 1H), 2.34 (dd, *J* = 18.6, 2.4 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.6, 159.9, 146.5, 145.7, 133.2, 132.1, 130.9, 130.1, 129.6, 127.4, 122.9, 118.8, 113.7, 51.9, 43.5; **HRMS(ESI-TOF)** m/z: $[M + H]^+$ $C_{17}H_{15}BrNO$calcd. 328.0337, found, 328.0318

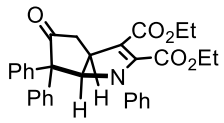
4. General procedure for the formal [3+2]-annulation to aza-bicyclo-[3,3,0]octanes (3-22)



4-aminocyclopentenone **1** (1.0 equiv.) and alkyne **2** (1.2 equiv.) were taken in HFIP (0.1M) and stirred at room temperature. Progress of the reaction was monitored through TLC analysis and upon completion (*ca*. 12-16h), the crude was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding [3+2] annulation products **3-22**.

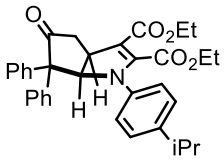
5. Characterization of [3+2] annulation products (3-22)

Diethyl-5-oxo-1,6,6-triphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (3)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.025g, 0.14 mmol,1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as semi-solid (red) in 94% (0.057 g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 5H), 6.92 - 6.83 (m,8H), 6.56 (dd, *J* = 7.8, 1.7 Hz, 2H), 5.83 (d, *J* = 10.3 Hz, 1H), 4.28 - 4.12 (m, 3H), 4.06 - 3.97 (m, 2H), 2.95 (dd, *J* = 19.5, 10.4 Hz, 1H), 2.60 (dd, *J* = 19.5, 4.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.6, 164.5, 162.4, 153.2, 141.3, 140.0, 139.4, 131.1, 129.0, 128.5, 128.0 (2), 127.4, 126.9, 125.7, 124.5, 107.1, 75.5, 67.0, 62.0, 60.1, 42.0, 38.8, 14.4, 13.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{31}H_{29}NNaO_5$calcd. 518.1943, found, 518.1938.

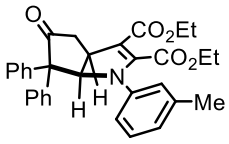
Diethyl-1-(4-isopropylphenyl)-5-oxo-6,6-diphenyl-1,3a,4,5,6,6a hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (4)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1b** (0.040g, 0.11 mmol, 1.0 equiv), Diethyl acetylene dicarboxylate **2a** (0.023g, 0.13 mmol, 1.2 equiv) in presence of HFIP. The crude was

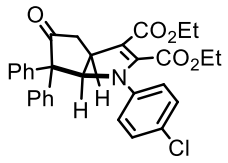
then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as semi-solid (colorless) in 79% (0.046 g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 5H), 6.89 - 6.84 (m, 5H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 5.78 (d, *J* = 10.2 Hz, 1H), 4.26 - 4.12 (m, 3H), 4.08 - 3.94 (m, 2H), 2.94 (dd, *J* = 19.5, 10.4 Hz, 1H), 2.68 (dt, *J* = 13.7, 6.8 Hz, 1H), 2.57 (dd, *J* = 19.5, 4.4 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.09 (dd, *J* = 6.9, 2.7 Hz, 6H), 0.94 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.6, 164.5, 162.4, 153.5, 146.4, 140.2, 139.42, 138.9, 131.0, 128.9, 128.0, 127.9, 127.3, 126.8, 126.4, 124.6, 106.6, 75.8, 66.8, 61.8, 60.1, 42.1, 38.6, 33.6, 24.0, 23.9, 14.4, 13.6; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{34}H_{36}NO_5$calcd. 538.2593, found, 538.2594.

Diethyl 5-oxo-6,6-diphenyl-1-(m-tolyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (5)



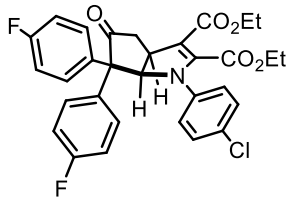
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1c** (0.040g, 0.12 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.025g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as semi-solid (colorless) in 68% (0.041g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 - 7.26 (m, 3H), 7.23 - 7.19 (m, 1H), 6.87 - 6.81 (m, 3H), 6.79 - 6.74 (m, 3H), 6.63 -6.61 (m, 1H), 6.44 - 6.42 (m, 1H), 6.10 (s, 1H), 5.72 (d, *J* = 10.3 Hz, 1H), 4.21 - 4.14 (m, 1H), 4.13 - 4.05 (m, 2H), 4.00 - 3.92 (m, 2H), 2.88 (dd, *J* = 19.5, 10.4 Hz, 1H), 2.52 (dd, *J* = 19.5, 4.1 Hz, 1H), 1.97 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.8, 164.5, 162.4, 153.3, 141.1, 140.1, 139.4, 138.2, 131.0, 129.0, 128.3, 128.0, 127.9, 127.2, 126.7, 126.6, 125.7, 121.2, 106.7, 75.7, 67.0, 61.9, 60.0, 42.0, 38.8, 21.0, 14.4, 13.7; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{32}H_{32}NO_5$calcd. 510.2280, found, 510.2272.

Diethyl 1-(4-chlorophenyl)-5-oxo-6,6-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (6)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1d** (0.050g, 0.14 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.029g, 0.17 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as semi-solid (yellow) in 72% (0.053g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 - 7.29 (m, 5H), 7.00 - 6.83 (m, 7H), 6.51 - 6.48 (m, 2H), 5.74 (d, *J* = 10.2 Hz, 1H), 4.27 - 4.12 (m, 3H), 4.04 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.94 (dd, *J* = 19.5, 10.5 Hz, 1H), 2.57 (dd, *J* = 19.5, 4.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.2, 164.3, 162.2, 152.6, 140.1, 139.8, 139.5, 131.2, 131.1, 129.1, 128.6, 128.1, 128.0, 127.5, 127.0, 125.9, 107.9, 75.8, 66.9, 62.2, 60.2, 41.9, 38.8, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{31}H_{29}ClNO_5$calcd. 530.1734, found, 530.1721.

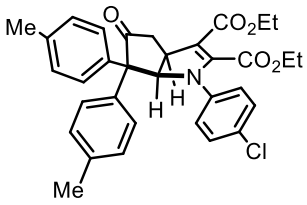
Diethyl 1-(4-chlorophenyl)-6,6-bis(4-fluorophenyl)-5-oxo-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (7)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1e** (0.040g, 0.10 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.021g, 0.12 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography(8:2

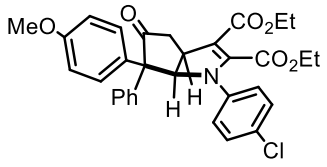
Hexane/EtOAc) to give the desired products as semi-solid (colorless) in 65% (0.037 g) yield; R_f 0.3 (EtOAc : Hexane 1:9); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.79 (dd, *J* = 8.3, 5.3 Hz, 2H), 6.63 (t, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 5.67 (d, *J* = 10.2 Hz, 1H), 4.23 - 4.14 (m, 3H), 4.07 - 4.01 (m, 2H), 2.93 (dd, *J* = 19.7, 10.5 Hz, 1H), 2.56 (dd, *J* = 19.7, 4.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (200 MHz, $CDCl_3$) δ 213.8, 164.2, 163.1, 162.5, 162.1, 161.8, 161.2, 152.5, 139.9, 135.5, 135.4, 135.1(2), 132.7, 132.6, 131.6, 129.7(2), 128.8, 125.8, 116.2, 116.1, 114.5, 114.4, 108.0, 75.8, 65.7, 62.3, 60.4, 41.7, 38.6, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{31}H_{26}ClF_2NNaO_5$ calcd. 588.1365, found, 588.1349.

Diethyl 1-(4-chlorophenyl)-5-oxo-6,6-di-p-tolyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (8)



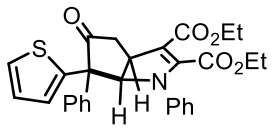
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1f** (0.040g, 0.10 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.021g, 0.12 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as oil in 81% (0.044 g) yield; R_f 0.25 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 - 7.20 (m, 2H), 7.15 - 7.13 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.72 - 6.68 (m, 4H), 6.50 (d, *J* = 8.7 Hz, 2H), 5.70 (d, *J* = 10.2 Hz, 1H), 4.22 - 4.12 (m, 3H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.94 (dd, *J* = 19.5, 10.5 Hz, 1H), 2.51 (dd, *J* = 19.5, 4.4 Hz, 1H), 2.32 (s, 3H), 2.15 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.3, 164.4, 162.3, 152.5, 140.0, 137.9, 136.9, 136.8, 136.4, 131.0, 130.9, 129.7, 128.3, 128.2, 127.8, 126.0, 107.8, 76.0, 66.3, 62.2, 60.2, 41.9, 38.5, 21.1, 20.9, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{33}H_{32}ClNNaO_5$calcd. 580.1867, found, 580.1867.

Diethyl 1-(4-chlorophenyl)-6-(4-methoxyphenyl)-5-oxo-6-phenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (9)



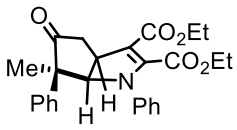
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1g** (0.040g, 0.10 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.021g,0.12 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless sticky solid in 64%(0.037 g) yield and isolated as inseparable mixture of diastereomer (1:1); R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.19 - 7.15 (m, 3H), 6.90 - 6.76 (m, 11H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.48 - 6.35 (m, 5H), 5.63 (dd, *J* = 19.1, 10.2 Hz, 2H), 4.18 - 4.05 (m, 6H), 4.01 - 3.94 (m, 4H), 3.72 (s, 3H), 3.59 (s, 2H), 2.87 (td, *J* = 19.5, 9.5 Hz, 2H), 2.47 (dt, *J* = 19.5, 4.7 Hz, 2H), 1.16 - 1.15 (m, 6H), 0.98 (td, *J* = 7.1, 3.8 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.4, 214.3, 164.4, 162.3(2), 159.3, 158.6, 152.6, 152.5, 140.1, 140.0, 139.6, 132.1, 131.6(2), 131.2, 131.1, 131.0, 129.2, 129.1, 128.6, 128.5, 128.1, 127.9, 127.5, 127.0, 125.9(2), 114.4, 113.0, 107.9, 107.8, 76.2 (2), 66.3, 66.2, 62.2(2), 60.2, 55.4, 55.3, 41.9(2), 38.7, 38.5, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{32}H_{30}ClNNaO_6$calcd. 582.1659, found, 582.1658.

Diethyl 5-oxo-1,6-diphenyl-6-(thiophen-2-yl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (10)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1h** (0.030g, 0.09 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.019g, 0.11 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless semi-solid in 53% (0.024g) yield and isolated as inseparable mixture of diastereomer (2:1); R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 - 7.30 (m, 3H), 7.03 - 7.00 (m, 2.73H), 6.98 - 6.89 (m, 6.49H), 6.87 - 6.85 (m, 2H), 6.77 (d, *J* = 7.3 Hz, 0.73H), 6.56 - 6.52 (m, 2.52H), 5.80 - 5.77 (m, 1.26H), 4.29 - 4.11 (m, 4.38H), 4.07 - 4.00 (m, 2.52H), 3.12 (dd, *J* = 19.7, 10.1 Hz, 1H), 2.92 (dd, *J* = 19.2, 10.6 Hz, 0.46H), 2.75 (dd, *J* = 19.5, 4.4 Hz, 1H), 2.55 (dd, *J* = 19.4, 3.8 Hz, 0.44H), 1.26 - 1.22 (m, 6.27H), 1.04 - 0.99 (m, 3.55H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.2, 212.4, 164.5, 164.4, 162.4, 162.3, 153.5, 152.6, 143.7, 140.9, 139.1, 130.4, 130.3, 129.6, 129.2, 128.6, 128.4, 127.5(2), 127.4, 127.1, 126.2, 126.1(2), 125.6(2), 124.9, 123.9, 107.3, 107.1, 75.9, 65.0, 63.8, 62.1, 62.0, 60.2, 42.1, 41.2, 39.4, 38.4, 29.8(2), 14.5(2), 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{27}NNaO_5$Scalcd. 524.1508, found, 524.1506.

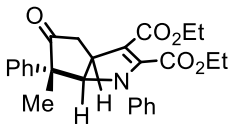
Diethyl (3aS,6S,6aR)-6-methyl-5-oxo-1,6-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (11)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1i** (0.040g, 0.15 mmol, 1.0 equiv), diethyl acetylene

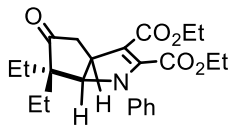
dicarboxylate **2a** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as colorless semi-solid in 96% (0.063g) yield (single diastereomer); R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 - 7.02 (m, 3H), 6.97 - 6.87 (m, 5H), 6.44 (d, *J* = 7.1 Hz, 2H), 5.03 (d, *J* = 11.1 Hz, 1H), 4.23 - 4.10 (m, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.16 (dd, *J* = 20.0, 9.7 Hz, 1H), 2.86 (dd, *J* = 20.0, 5.6 Hz, 1H), 1.54 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 219.9, 164.7, 162.4, 151.9, 140.6, 138.3, 128.6, 128.4, 127.8, 127.1, 125.2, 123.1, 106.7, 77.6, 62.0, 59.9, 58.0, 43.2, 38.8, 24.7, 14.4, 13.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{27}NNaO_5$calcd. 456.1787, found, 456.1780.

Diethyl (3aS,6R,6aR)-6-methyl-5-oxo-1,6-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (12)



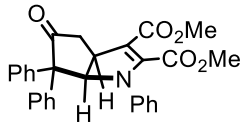
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1j** (0.040g, 0.15 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as white powder in 82% (0.054g) yield (single diastereomer); R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 2H), 7.23 - 7.16 (m, 3H), 7.08 - 7.03 (m, 3H), 6.97 (d, *J* = 7.7 Hz, 2H), 5.28 (d, *J* = 10.6 Hz, 1H), 4.21 - 4.00 (m, 5H), 2.93 (dd, *J* = 19.7, 10.1 Hz, 1H), 2.76 (dd, *J* = 19.7, 4.8 Hz, 1H), 1.31 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 218.1, 164.4, 162.7, 151.0, 142.7, 141.8, 129.4, 129.1, 127.4, 126.1, 125.5, 122.2, 108.7, 76.7, 62.3, 60.1, 58.8, 41.8, 39.2, 19.9, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$$C_{26}H_{27}NNaO_5$calcd. 456.1787, found, 456.1790.

Diethyl 6,6-diethyl-5-oxo-1-phenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (13)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1k** (0.040g, 0.17 mmol, 1.0 equiv), diethyl acetylene dicarboxylate **2a** (0.036g, 0.20 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as white semi-solid in 79% (0.055g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 - 7.29 (m, 2H), 7.21 - 7.16 (m, 3H), 4.90 (d, *J* = 11.4 Hz, 1H), 4.19 - 4.08 (m, 4H), 3.97 - 3.90 (m, 1H), 2.80 (dd, *J* = 19.3, 9.9 Hz, 1H), 2.52 (dd, *J* = 19.3, 6.6 Hz, 1H), 1.64 (ddd, *J* = 27.6, 14.5, 7.4 Hz, 2H), 1.40 (dt, *J* = 14.6, 7.4 Hz, 1H), 1.33 - 1.25 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.69 (t, *J* = 7.4 Hz, 3H), 0.54 (t, *J* = 7.5 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 219.0, 164.7, 162.7, 152.5, 142.0, 129.5, 126.6, 124.5, 107.7, 73.3, 62.1, 59.9, 57.9, 42.7, 38.4, 27.0, 23.5, 14.4, 13.8, 8.3, 8.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{23}H_{29}NNaO_5$calcd. 422.1943, found, 422.1942.

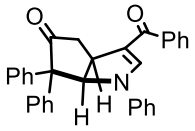
Dimethyl 5-oxo-1,6,6-triphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (14)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), dimethyl acetylene dicarboxylate **2b** (0.021g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a white sticky solid in 94% (0.054g)

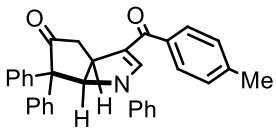
yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 - 7.29 (m, 5H), 6.93 - 6.86 (m, 6H), 6.83 - 6.81 (m, 2H), 6.55 - 6.53 (m, 2H), 5.86 (d, *J* = 10.4 Hz, 1H), 4.25 (td, *J* = 10.4, 4.1 Hz, 1H), 3.70 (s, 3H), 3.58 (s, 3H), 2.94 (dd, *J* = 19.4, 10.4 Hz, 1H), 2.58 (dd, *J* = 19.4, 4.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.5, 164.9, 162.9, 153.3, 141.1, 139.9, 139.3, 131.0, 129.0, 128.6, 128.0, 127.4, 126.9, 125.6, 124.0, 107.0, 75.3, 67.0, 52.8, 51.5, 42.0, 38.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{29}H_{25}NNaO_5$calcd. 490.1630, found, 490.1625.

2-Benzoyl-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (15)



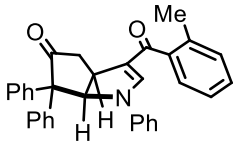
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), alkyne derivative **2c** (0.020g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 73% (0.041g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.2 Hz, 2H), 7.55 - 7.42 (m, 9H), 6.99 - 6.96 (m, 5H), 6.88 - 6.83 (m, 3H), 6.57 (d, *J* = 5.3 Hz, 2H), 6.06 (d, *J* = 9.2 Hz, 1H), 4.49 (s, 1H), 3.12 - 3.09 (m, 1H), 2.92 (d, *J* = 19.2 Hz, 1H); **^{13}C{^{1}H} NMR** (200 MHz, $CDCl_3$) δ 215.4, 190.1, 150.4, 141.1, 140.5, 139.6, 138.9, 131.4, 131.0, 129.2, 128.9, 128.5, 128.2, 128.1(2), 127.2, 127.1, 123.0, 120.3, 117.6, 70.7, 67.5, 41.0, 39.9; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{32}H_{26}NO_2$calcd. 456.1964, found, 456.1960.

2-(4-Methylbenzoyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (16)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), alkyne derivative **2d** (0.022g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 38% (0.022g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 - 7.47 (m, 4H), 7.45 - 7.39 (m, 3H), 7.24 - 7.21 (m, 3H), 6.96 - 6.89 (m, 5H), 6.84 -6.81 (m, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 2H), 5.99 (d, *J* = 10.2 Hz, 1H), 4.44 (td, *J* = 10.0, 1.8 Hz, 1H), 3.05 (dd, *J* = 19.2, 10.0 Hz, 1H), 2.86 (dd, *J* = 19.2, 2.5 Hz, 1H), 2.40 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.5, 190.0, 149.9, 141.5, 141.2, 139.7, 139.0, 137.8, 131.5, 130.2, 129.9, 129.2, 128.9, 128.2(2), 127.2, 127.1, 122.9, 120.4, 117.5, 70.7, 67.6, 41.0, 40.1, 21.6; **HRMS(ESI-TOF)** m/z: $[M + H]^+$ $C_{33}H_{28}NO_2$calcd. 470.2120, found, 470.2116.

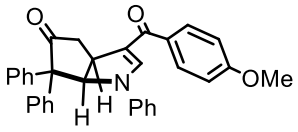
2-(2-methylbenzoyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (17)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), alkyne derivative **2e** (0.022g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 63% (0.036g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 - 7.49 (m, 2H), 7.45 - 7.38 (m, 3H), 7.32 - 7.28

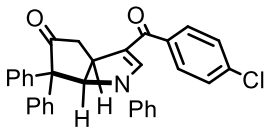
(m, 1H), 7.24 - 7.19 (m, 3H), 6.95 (s, 1H), 6.92 - 6.84 (m, 5H), 6.79 - 6.74 (m, 3H), 6.47 (d, *J* = 7.9 Hz, 2H), 6.05 (d, *J* = 10.3 Hz, 1H), 4.43 (td, *J* = 10.2, 2.2 Hz, 1H), 3.07 (dd, *J* = 19.2, 10.2 Hz, 1H), 2.88 (dd, *J* = 19.1, 2.5 Hz, 1H), 2.37 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 215.2, 192.1, 151.3, 141.0, 140.4, 139.6, 138.8, 135.7, 131.5, 131.0, 129.3, 129.2, 128.8, 128.3, 128.1, 127.3, 127.1, 125.3, 123.1, 121.7, 117.9, 71.0, 67.5, 41.1, 38.9, 19.7; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{33}H_{28}NO_2$calcd. 470.2120, found, 470.2113.

2-(4-methoxybenzoyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (18)



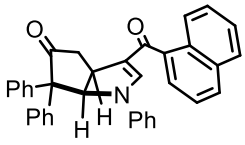
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.050g, 0.15 mmol, 1.0 equiv), alkyne derivative **2f** (0.030g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 48% (0.036g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 - 7.56 (m, 2H), 7.51 - 7.49 (m, 2H), 7.44 - 7.37 (m, 3H), 7.21 (s, 1H), 6.97 - 6.90 (m, 7H), 6.85 - 6.82 (m, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 2H), 5.98 (d, *J* = 10.2 Hz, 1H), 4.44 (td, *J* = 10.0, 1.9 Hz, 1H), 3.86 (s, 3H), 3.05 (dd, *J* = 19.2, 10.0 Hz, 1H), 2.85 (dd, *J* = 19.2, 2.5 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 215.5, 162.1, 149.3, 141.3, 139.7, 139.0, 133.1, 131.4, 130.1, 129.2, 128.9, 128.2(2), 127.2, 127.1, 122.8, 120.3, 117.4, 113.7, 70.6, 67.5, 55.6, 41.0, 40.3; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{33}H_{28}NO_3$calcd. 486.2069, found, 486.2058.

2-(4-Chlorobenzoyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (19)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1 equiv), alkyne derivative **2g** (0.025g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 58% (0.035g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 - 7.48 (m, 4H), 7.45 - 7.38 (m, 5H), 7.17 (s, 1H), 6.97 - 6.89 (m, 5H), 6.83 - 6.78 (m, 3H), 6.52 (d, *J* = 7.8 Hz, 2H), 6.01 (d, *J* = 10.2 Hz, 1H), 4.43 (td, *J* = 10.2, 2.0 Hz, 1H), 3.05 (dd, *J* = 19.2, 10.0 Hz, 1H), 2.85 (dd, *J* = 19.2, 2.5 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.2, 188.6, 150.4, 141.0, 139.6, 138.9, 138.8, 137.1, 131.4, 129.5, 129.2, 129.0, 128.8, 128.2, 128.1, 127.3, 127.2, 123.2, 120.2, 117.7, 70.9, 67.5, 40.9, 39.9; **HRMS(ESI-TOF)** m/z: $[M + H]^+$ $C_{32}H_{25}ClNO_2$calcd. 490.1574, found, 490.1560.

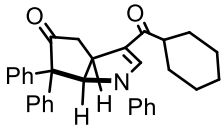
2-(1-Naphthoyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (20)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.050g, 0.15 mmol, 1.0 equiv), alkyne derivative **2h** (0.034g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 57% (0.044g) yield; R_f 0.25 (EtOAc : Hexane

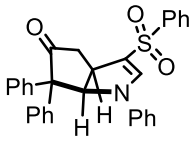
2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 - 8.12 (m, 1H), 7.92 - 7.87 (m, 2H), 7.57 - 7.50 (m, 4H), 7.47 - 7.39 (m, 5H), 7.01 (s, 1H), 6.89 - 6.83 (m, 5H), 6.81 - 6.78 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 2H), 6.09 (d, *J* = 10.3 Hz, 1H), 4.54 (td, *J* = 10.0, 2.5 Hz, 1H), 3.15 (dd, *J* = 19.1, 9.9 Hz, 1H), 3.03 (dd, *J* = 19.1, 2.7 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.2, 191.3, 151.6, 140.8, 139.6, 138.7, 138.4, 133.9, 131.4, 130.7, 130.0, 129.2, 128.7, 128.3, 128.2, 128.1, 127.1, 127.0, 126.5, 125.7, 125.4, 124.6, 123.2, 122.3, 117.9, 71.1, 67.5, 41.1, 39.1; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{36}H_{28}NO_2$calcd. 506.2120, found, 506.2111.

2-(Cyclohexanecarbonyl)-1,6,6-triphenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (21)



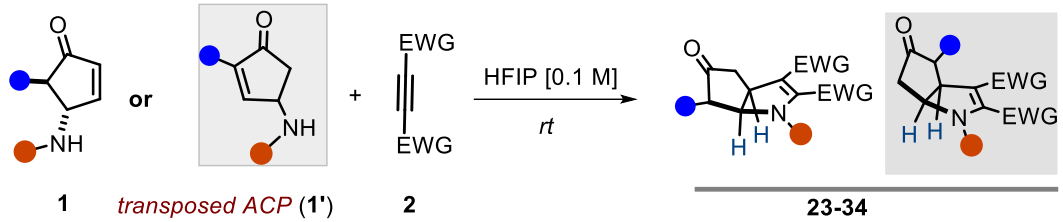
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.050g, 0.15 mmol, 1.0 equiv), alkyne derivative **2i** (0.026g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (9:1 Hexane/EtOAc) to give the desired products as a colorless liquid in 35% (0.025g) yield; R_f 0.25 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 - 7.47 (m, 2H), 7.43 - 7.36 (m, 5H), 6.97 - 6.93 (m, 2H), 6.87 - 6.85 (m, 2H), 6.79 - 6.74(m, 3H), 6.57 (d, *J* = 7.8 Hz, 2H), 5.91 (d, *J* = 10.3 Hz, 1H), 4.21 (td, *J* = 10.4, 2.5 Hz, 1H), 2.95 (dd, *J* = 19.2, 10.4 Hz, 1H), 2.66 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.58 (dd, *J* = 19.2, 2.8 Hz, 1H), 1.86 - 1.77 (m, 2H), 1.73 - 1.67 (m, 3H), 1.55 - 1.49 (m, 2H), 1.31 - 1.26 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.3, 198.7, 146.7, 141.7, 139.5, 139.0, 131.5, 129.1, 128.7, 128.2, 128.1, 127.1, 122.7, 120.2, 117.9, 70.3, 67.5, 46.6, 41.4, 38.9, 30.3, 30.0, 26.2, 26.0(2); **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{32}H_{32}NO_2$calcd. 462.2433, found, 462.2425.

1,6,6-Triphenyl-2-(phenylsulfonyl)-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (22)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), alkyne derivative **2j** (0.025g, 0.14 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 68% (0.041g) yield; R_f 0.4 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 2H), 7.62 - 7.59 (m, 1H), 7.56 - 7.53 (m, 2H), 7.44 (s, 1H), 7.42 - 7.34 (m, 5H), 6.93 (t, *J* = 7.9 Hz, 2H), 6.88 - 6.81 (m, 3H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.70 - 6.68 (m, 2H), 6.50 (d, *J* = 7.8 Hz, 2H), 5.98 (d, *J* = 10.3 Hz, 1H), 4.04 - 3.98 (m, 1H), 2.71 - 2.69 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 213.8, 148.2, 142.0, 141.1, 138.9, 138.4, 133.0, 131.4, 129.4, 129.2, 128.8, 128.3, 128.0, 127.2, 127.1, 122.9, 117.6, 115.2, 71.7, 66.7, 40.2, 39.4; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{31}H_{26}NO_3$Scalcd. 492.1633, found, 492.1614.

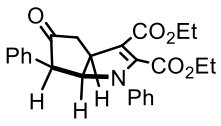
6. General procedure for the formal [3+2] annulation to aza-bicyclo-[3,3,0]octanes (23-34) *[with the use of mono substituted 4-aminocyclopentenones and transposed variants]*



4-aminocyclopentenone **1** or **1'** (1.0 equiv.) and alkyne **2** (1.2 equiv.) were taken in HFIP (0.1M) and stirred at room temperature until complete disappearance of the starting material was observed by TLC (*ca*. 12-16 h). The crude was then concentrated and the residue was purified by silica gel column chromatography to give the desired [3+2] annulation products (**23-34**). [Note: when the transposed version of 4-aminocyclopentenones (**1**') were used, the relative spatial orientation between the substituent at α-position to carbonyl group and that on the nitrogen-atom, was *anti* in the final products].

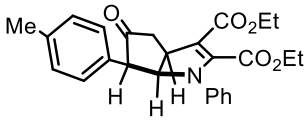
7. Experimental details and characterization of [3+2] annulation products (23-34)

Diethyl 5-oxo-1,6-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (23)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1l** (0.040g, 0.16 mmol, 1.0 equiv), alkyne derivative **2a** (0.033g, 0.19 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 66% (0.045g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (m, 4H), 7.28 - 7.26 (m, 1H), 7.20 - 7.16 (m, 3H), 7.10 (d, *J* = 7.7 Hz, 2H), 5.21 - 5.16 (m, 1H), 4.30 - 4.22 (m, 2H), 4.11 - 3.97 (m, 3H), 3.75 (d, *J* = 6.5 Hz, 1H), 2.87 - 2.80 (dd, *J* = 19.3, 7.7 Hz, 1H), 2.70-2.66 (d, *J* = 19.3 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.9, 164.6, 162.7, 150.1, 139.3, 138.6, 129.7, 128.9, 128.1, 127.3, 125.9, 122.4, 108.2, 65.0, 62.5, 61.1, 59.9, 49.9, 42.4, 14.0, 13.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{25}H_{25}NNaO_5$calcd. 442.1630, found, 442.1626.

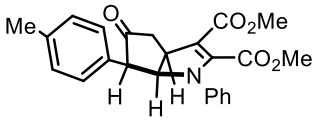
Diethyl 5-oxo-1-phenyl-6-(p-tolyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (24)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1m** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2a** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 84% (0.055g) yield;

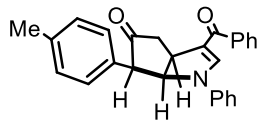
R_f 0.3 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 2H), 7.12 - 7.09 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.10 (dd, *J* = 10.4, 3.0 Hz, 1H), 4.30 - 4.15 (m, 4H), 4.14 - 4.06 (m, 1H), 3.57 (brs, 1H), 2.99 (dd, *J* = 19.7, 10.1 Hz, 1H), 2.73 - 2.67 (m, 1H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.3, 164.6, 162.7, 149.2, 139.3, 137.3, 134.3, 129.9, 129.5, 127.4, 125.6, 122.4, 108.4, 73.5, 62.4, 60.0, 60.0, 43.3, 40.2, 21.1, 14.5, 13.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{26}H_{27}NNaO_5$calcd. 456.1787, found, 456.1783.

Dimethyl 5-oxo-1-phenyl-6-(p-tolyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (25)



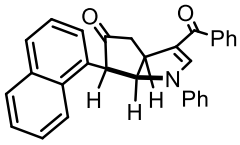
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1m** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2b** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 78% (0.049g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 - 7.24 (m, 2H), 7.15 - 7.12 (m, 3H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.14 (dd, *J* = 10.4, 2.9 Hz, 1H), 4.11 (td, *J* = 10.3, 6.1 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.58 (s, 1H), 3.02 (dd, *J* = 19.7, 10.1 Hz, 1H), 2.70 (ddd, *J* = 19.7, 5.8, 0.9 Hz, 1H), 2.33 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.1, 165.0, 163.2, 149.3, 139.1, 137.4, 134.2, 129.9, 129.6, 127.4, 125.6, 122.0, 108.5, 73.5, 58.9, 53.2, 51.5, 43.3, 40.1, 21.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{24}H_{23}NNaO_5$calcd. 428.1474, found, 428.1471.

2-Benzoyl-1-phenyl-6-(p-tolyl)-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (26)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1m** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2c** (0.024g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 80% (0.048 g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 - 7.48 (m, 2H), 7.36 - 7.26 (m, 4H), 7.08 - 7.03 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.95 (dd, *J* = 10.4, 2.7 Hz, 1H), 4.23 (m, 1H), 3.37 (s, 1H), 3.02 (dd, *J* = 19.8, 10.4 Hz, 1H), 2.55 (dd, *J* = 19.7, 3.3 Hz, 1H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.2, 190.3, 146.3, 140.6, 139.4, 137.7, 134.6, 131.0, 130.2, 129.8, 128.6, 128.1, 127.4, 123.3, 121.1, 116.5, 70.3, 59.5, 43.0, 40.8, 21.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{27}H_{24}NO_{23}$calcd 394.1807, found, 394.1802.

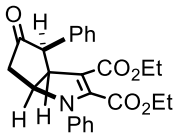
2-benzoyl-6-(naphthalen-1-yl)-1-phenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (27)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1n** (0.042g, 0.14 mmol, 1.0 equiv), alkyne derivative **2c** (0.022g, 0.17 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 68% (0.041g) yield; R_f 0.4 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 - 7.83 (m, 3H), 7.73 - 7.71 (m, 2H), 7.61 (s, 1H),

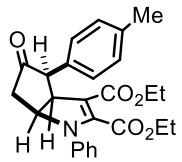
7.54 - 7.47 (m, 6H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 5.37 (dd, *J* = 10.5, 3.1 Hz, 1H), 4.59 (td, *J* = 10.4, 4.7 Hz, 1H), 4.39 (s, 1H), 3.38 (dd, *J* = 19.7, 10.4 Hz, 1H), 2.83 (dd, *J* = 19.7, 4.0 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 214.4, 190.3, 146.4, 140.6, 139.4, 134.4, 134.0, 131.1 (2), 129.8, 129.2, 128.8, 128.6, 128.1, 126.9, 126.3, 125.6, 123.9, 123.3, 121.1, 116.5, 70.6, 43.0, 40.8; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{30}H_{24}NO_2$calcd. 430.1807, found, 430.1806.

Diethyl 5-oxo-1,4-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (28)



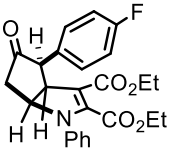
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'a** (0.035g, 0.14 mmol, 1.0 equiv), alkyne derivative **2a** (0.028g, 0.17 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 54% (0.032g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 4H), 7.24 (s, 1H), 7.16 (m, 3H), 7.08 (d, *J* = 7.7 Hz, 2H), 5.17 (ddd, *J* = 10.2, 7.8, 2.5 Hz, 1H), 4.24 (pd, *J* = 7.6, 3.6 Hz, 2H), 4.05 - 3.95 (m, 3H), 3.73 (d, *J* = 6.5 Hz, 1H), 2.85 -2.78 (m, 1H), 2.69 - 2.64 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 214.9, 164.6, 162.7, 150.1, 139.3, 138.6, 129.7, 128.9, 128.1, 127.3, 125.9, 122.4, 108.2, 65.0, 62.5, 61.1, 59.9, 50.0, 42.4, 14.1, 13.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{25}H_{25}NNaO_5$calcd. 442.1630, found, 442.1630.

Diethyl 5-oxo-1-phenyl-4-(p-tolyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (29)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'b** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2a** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 69% (0.046g) yield; R_f 0.4 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 2H), 7.19 - 7.14 (dd, *J* = 14.2, 7.5 Hz, 3H), 7.10 - 7.07 (t, *J* = 6.4 Hz, 4H), 5.17 (t, *J* = 7.8 Hz, 1H), 4.29 - 4.22 (m, 2H), 4.06 - 3.97 (m, 3H), 3.71 (d, *J* = 6.2 Hz, 1H), 2.82 (dd, *J* = 19.3, 7.7 Hz, 1H), 2.66 (d, *J* = 19.2 Hz, 1H), 2.32 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.1, 164.6, 162.7, 150.0, 139.3, 136.9, 135.7, 129.7, 129.6, 127.8, 125.8, 122.4, 108.2, 64.9, 62.5, 60.7, 59.9, 50.1, 42.3, 21.2, 14.1, 13.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{26}H_{27}NNaO_5$calcd. 456.1787, found, 456.1787.

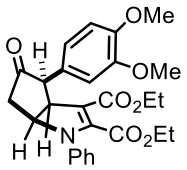
Diethyl 4-(4-fluorophenyl)-5-oxo-1-phenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (30)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'c** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2a** (0.031g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 53% (0.035g) yield;

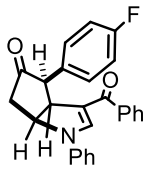
R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.20 - 7.14 (m, 3H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.19 - 5.15 (m, 1H), 4.29 - 4.21 (m, 2H), 4.02 - 3.96 (m, 3H), 3.72 (d, *J* = 7.1 Hz, 1H), 2.80 (dd, *J* = 19.4, 7.5 Hz, 1H), 2.71 - 2.66 (d, *J* = 19.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.6, 164.5, 163.3, 162.6, 160.8, 150.2, 139.1, 134.1, 129.7(2), 126.0, 122.5, 115.8, 115.6, 108.2, 64.8, 62.5, 60.4, 59.9, 49.8, 42.2, 14.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.62(s); **HRMS(ESI-TOF)** m/z: [M + Na]$^+$$C_{25}H_{24}FNNaO_5$calcd. 460.1536, found, 460.1540.

Diethyl 4-(3,4-dimethoxyphenyl)-5-oxo-1-phenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (31)



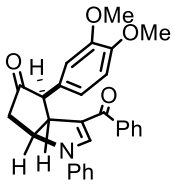
Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'd** (0.040g, 0.13 mmol, 1.0 equiv), alkyne derivative **2a** (0.027g, 0.16 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 63% (0.039g) yield; R_f 0.25 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10 - 7.08 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.75 - 6.70 (m, 2H), 5.16 (ddd, *J* = 10.1, 7.8, 2.4 Hz, 1H), 4.25 (dtt, *J* = 10.8, 7.4, 3.6 Hz, 2H), 4.06 - 3.98(m, 3H), 3.86 (d, *J* = 9.7 Hz, 6H), 3.69 (d, *J* = 6.3 Hz, 1H), 2.82 (dd, *J* = 19.3, 7.7 Hz, 1H), 2.65 (d, *J* = 19.3 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.0, 164.6, 162.7, 150.0, 149.2, 148.4, 139.3, 131.0, 129.7, 125.9, 122.5, 119.7, 111.8, 111.5, 108.2, 64.9, 62.5, 60.5, 59.9, 56.1(2), 49.9, 42.2, 14.2, 13.9; **HRMS(ESI-TOF)** m/z: [M + Na]$^+$ $C_{27}H_{29}NNaO_7$calcd. 502.1842, found, 502.1836.

3-Benzoyl-4-(4-fluorophenyl)-1-phenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (32)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'c** (0.040g, 0.15 mmol, 1.0 equiv), alkyne derivative **2c** (0.024g, 0.18 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 60% (0.037g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.1 Hz, 2H), 7.56 (s, 1H), 7.53 - 7.43 (m, 3H), 7.37 - 7.30 (m, 4H), 7.10 - 7.04 (m, 3H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.23 - 5.17 (m, 1H), 4.35 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.90 (d, *J* = 2.7 Hz, 1H), 3.12 (dd, *J* = 19.3, 8.6 Hz, 1H), 2.65 (d, *J* = 19.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.2, 190.2, 163.3, 160.9, 146.0, 140.5, 139.4, 134.9 (2), 131.1, 130.1, 129.4, 129.3, 128.6, 128.1, 123.4, 120.0, 116.0, 115.9, 115.8, 61.2, 59.4, 50.9, 43.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.50 (s); **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{26}H_{21}FNO_2$calcd. 398.1556, found, 398.1557.

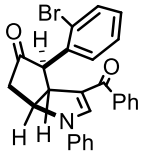
3-Benzoyl-4-(3,4-dimethoxyphenyl)-1-phenyl-3a,4,6,6a tetrahydrocyclopenta[b]pyrrol-5(1H)-one (33)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'd** (0.040g, 0.13 mmol, 1.0 equiv), alkyne derivative **2c** (0.021g, 0.16 mmol, 1.2 equiv) in presence of HFIP. The crude was then

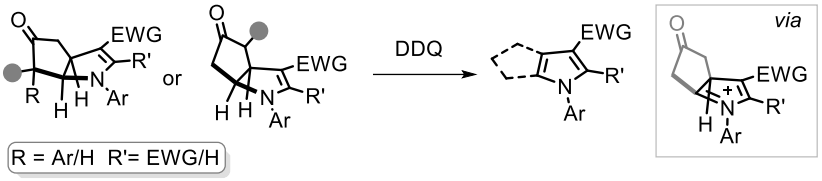
concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 61% (0.035g) yield; R_f 0.3 (EtOAc : Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 2H), 7.55 (s, 1H), 7.52 - 7.43 (m, 3H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 1.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.86 - 6.80 (m, 2H), 5.23 - 5.12 (m, 1H), 4.39 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.92 - 3.89 (m, 4H), 3.86 (s, 3H), 3.13 (dd, *J* = 19.1, 8.7 Hz, 1H), 2.62 - 2.55 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 215.4, 190.3, 149.4, 148.4, 145.9, 140.6, 139.4, 131.7, 131.0, 130.0, 128.5, 128.1, 123.3, 119.8, 118.7, 115.8, 111.7, 111.4, 61.3, 59.3, 56.1, 56.0, 50.8, 42.9; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{28}H_{26}NO_4$calcd. 440.1862, found, 440.1858.

3-Benzoyl-4-(2-bromophenyl)-1-phenyl-3a,4,6,6a-tetrahydrocyclopenta[b]pyrrol-5(1H)-one (34)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1'e** (0.040g, 0.12 mmol, 1.0 equiv), alkyne derivative **2c** (0.020g, 0.15 mmol, 1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 84% (0.047g) yield; R_f 0.3 (EtOAc : Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.1 Hz, 2H), 7.58 - 7.54 (m, 2H), 7.50 - 7.43 (m, 3H), 7.38 - 7.32 (m, 4H), 7.18 - 7.15 (m, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 5.36 - 5.30 (m,1H), 4.41 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.98 (d, *J* = 6.4 Hz, 1H), 3.30 (dd, *J* = 19.2, 8.3 Hz, 1H), 2.71 (dd, *J* = 19.1, 5.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.3, 190.1, 145.7, 140.7, 139.5, 133.9, 133.1, 130.9, 130.0, 129.2, 128.5, 128.0, 127.8, 123.2, 122.8, 121.0, 115.8, 62.9, 62.0, 50.3, 44.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{20}BrNNaO_2$calcd. 480.0575, found, 480.0577.

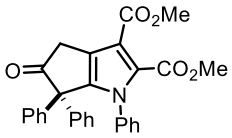
8. General Procedure of DDQ Oxidation (35-40)



Starting material (1.0 equiv.) was taken in toluene (0.1 M) and was added DDQ (1.5 equiv). The resulting mixture was stirred for 24 h at room temperature (TLC monitored). Solvent was removed in vacuo and crude residue was purified by silica-gel column chromatography to give fused pyrrole derivatives **35-40**.

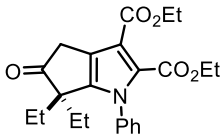
9. Experimental details and characterization of DDQ oxidation product (35-40)

Dimethyl 5-oxo-1,6,6-triphenyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (35)



Title compound was prepared according to the general procedure using annulation product **14** (0.040g, 0.08 mmol, 1.0 equiv) and DDQ (0.029g, 0.13 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 80% (0.032g) yield; R_f 0.5 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 - 7.12 (m, 7H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.91 - 6.89 (m, 4H), 6.67 - 6.64 (m, 2H), 3.89 (s, 3H), 3.66 (s, 2H), 3.63 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 212.9, 164.2, 161.5, 140.6, 139.5, 136.7, 130.5, 129.2, 128.7, 128.5, 128.2, 127.5, 121.2, 114.3, 67.0, 52.5, 52.0, 38.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{23}NNaO_5$calcd. 488.1474, found, 488.1471.

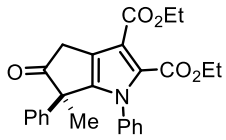
Diethyl 6,6-diethyl-5-oxo-1-phenyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (36)



Title compound was prepared according to the general procedure using annulation product **13** (0.039g, 0.10 mmol, 1.0 equiv) and DDQ (0.034g, 0.15 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colorless liquid in 76% (0.029g) yield; R_f 0.25 (EtOAc : Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ

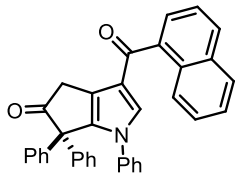
7.47 - 7.40 (m, 3H), 7.26 - 7.24 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 2H), 1.64 (dq, *J* = 14.7, 7.3 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 - 1.10 (m, 2H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.58 (t, *J* = 7.5 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 220.3, 164.0, 160.8, 139.8, 137.8, 129.4 (2), 129.1, 127.0, 122.8, 115.3, 61.3, 60.7, 59.8, 41.0, 30.6, 14.4, 13.8, 9.8; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{23}H_{28}NO_5$calcd. 398.1967, found, 398.1946.

Diethyl (R)-6-methyl-5-oxo-1,6-diphenyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (37)



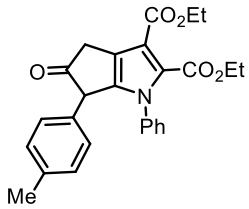
Title compound was prepared according to the general procedure using annulation product **11** (0.038g, 0.09 mmol, 1.0 equiv) and DDQ (0.030g, 0.13 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 71% (0.027g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 - 7.12 (m, 6H), 6.96 - 6.83 (m, 4H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.58 (q, *J* = 22.0 Hz, 2H), 1.35 - 1.31 (m, 6H), 0.99 (t, *J* = 7.1 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 214.2, 163.8, 160.9, 142.6, 140.5, 137.2, 129.8, 128.9, 128.8, 128.7, 127.4, 127.0, 126.4, 121.0, 114.9, 61.5, 60.7, 55.7, 38.3, 20.1, 14.4, 13.8; **HRMS(ESI-TOF)** m/z: $[M + H]^+$ $C_{26}H_{26}NO_5$calcd. 432.1811, found, 432.1806.

3-(1-Naphthoyl)-1,6,6-triphenyl-4,6-dihydrocyclopenta[b]pyrrol-5(1H)-one (38)



Title compound was prepared according to the general procedure using annulation product **20** (0.037g, 0.07 mmol, 1.0 equiv) and DDQ (0.025g, 0.11 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 60% (0.022g) yield; R_f 0.3 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 - 8.29 (m, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.91 - 7.89 (m, 1H), 7.79 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.57 - 7.50 (m, 3H), 7.21 - 7.13 (m, 8H), 7.06 - 7.01 (m, 6H), 6.70 (d, *J* = 7.5 Hz, 2H), 3.60 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 213.8, 140.1, 138.4, 138.1, 133.9, 132.6, 130.8, 130.6, 129.4, 128.9, 128.5, 128.3, 127.5, 127.2, 126.6, 126.3, 126.1, 125.8, 124.6, 122.9, 122.1, 66.6, 39.2; **HRMS(ESI-TOF)** m/z: $[M + H]^+C_{36}H_{26}NO_2$calcd. 504.1964, found, 504.1960.

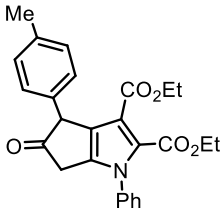
Dimethyl 5-oxo-1-phenyl-6-(p-tolyl)-1,4,5,6-tetrahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (39)



Title compound was prepared according to the general procedure using annulation product **24** (0.035g, 0.09 mmol, 1.0 equiv) and DDQ (0.030g, 0.13 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 68% (0.024g) yield; R_f 0.3 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ

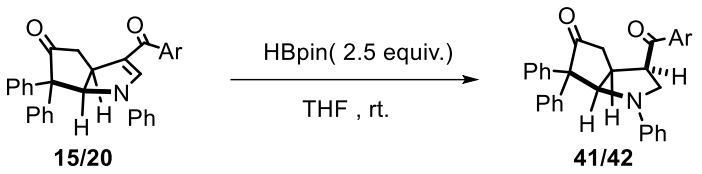
7.25 - 7.19 (m, 3H), 7.00 - 6.96 (m, 4H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.34 (s, 1H), 3.89 (s, 3H), 3.70 (s, 3H), 3.61 (d, *J* = 3.3 Hz, 2H), 2.24 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 211.5, 164.2, 161.6, 138.1, 137.4 (2), 133.0, 129.6, 129.4, 129.0, 128.6, 127.5, 125.8, 122.9, 115.0, 55.2, 52.5, 52.0, 39.6, 21.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{24}H_{21}NNaO_5$calcd. 426.1317, found, 426.1316.

Diethyl 5-oxo-1-phenyl-4-(p-tolyl)-1,4,5,6-tetrahydrocyclopenta[b]pyrrole-2,3-dicarboxylate (40)



Title compound was prepared according to the general procedure using annulation product **29** (0.030g, 0.09 mmol, 1.0 equiv) and DDQ (0.024g, 0.10 mmol, 1.5 equiv) in presence of Toluene. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colorless liquid in 44% (0.013g) yield; R_f 0.3 (EtOAc : Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 - 7.45 (m, 3H), 7.35 - 7.33 (m, 2H), 7.12 - 7.07 (m, 4H), 4.69 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.06 - 4.00 (m, 2H), 3.40 - 3.25 (m, 2H), 2.31 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 210.8, 163.3, 161.1, 138.2, 137.0, 135.6, 134.6, 129.6, 129.3, 128.8, 127.7, 125.6, 125.0, 116.6, 61.7, 60.5, 57.0, 37.7, 21.2, 13.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{25}NNaO_5$calcd. 454.1630, found, 454.1632.

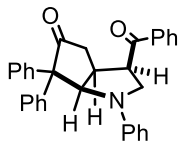
10. General procedure for the reduction of olefin[5]



Starting material (compound **15** or **20**; 1.0 equiv.) was taken in dry THF (0.1 M) and was added HBpin (2.5 equiv.). The reaction mixture was stirred for 10 min at room temperature (TLC monitored). Upon completion of the reaction, solvent was removed in vacuo and the crude residue was purified by silica-gel column chromatography to give the reduced products **41**/**42**.

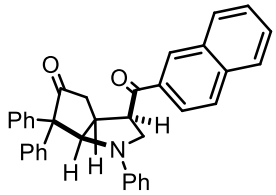
11. Characterization data of compounds 41-42

3-Benzoyl-1,6,6-triphenylhexahydrocyclopenta[b]pyrrol-5(1H)-one (41)



Following the general procedure, dihydropyrrole **15** (0.020g, 0.044 mmol) was converted to fully saturated compound **41** in 75% yield (0.015g; oil); eluent (n-hexanes/ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.63 (m, 1H), 7.59 – 7.52 (m, 4H), 7.49 – 7.45 (m, 2H), 7.41 – 7.37 (m, 1H), 6.84 – 6.80 (m, 3H), 6.77 – 6.73 (m, 2H), 6.69 – 6.67 (m, 2H), 6.36 (t, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 8.2 Hz, 2H), 5.54 (d, *J* = 5.8 Hz, 1H), 4.42 – 4.36 (m, 1H), 4.11 (t, *J* = 10.7 Hz, 1H), 3.73 – 3.69 (m, 1H), 3.58 – 3.49 (m, 1H), 2.36 – 2.24 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 214.8, 198.7, 148.9, 140.4, 137.9, 136.3, 133.6, 131.1, 128.9 (2), 128.6, 128.2, 127.9, 127.5, 126.2, 126.0, 116.4, 114.1, 69.2, 68.3, 52.6, 47.6, 36.2, 35.6; HRMS(ESI-TOF) m/z: $[M + H]^+C_{32}H_{27}NO_2$calcd. 458.2115, found, 458.2121.

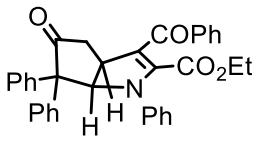
(2-Naphthoyl)-1,6,6-triphenylhexahydrocyclopenta[b]pyrrol-5(1H)-one (42)



Following the general procedure, dihydropyrrole **20** (0.017g, 0.034 mmol, 1.0 equiv) was converted to fully saturated compound **42** in 70% yield (012 g; oil); eluent (n-hexanes/ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, DMSO) δ 8.13 (t, *J* = 9.1 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.31 (m, 5H), 7.15-7.08 (m, 3H), 6.97 – 6.79 (m, 4H), 6.44 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 8.1 Hz, 2H), 5.47 (d, *J* = 7.4 Hz, 1H), 3.92-3.86 (m, 1H), 3.53 – 3.46 (m, 2H), 3.31 (d, *J* = 4.1 Hz, 1H), 2.94-2.86 (m, 1H), 2.65-2.60 (m,1H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO) δ 217.1, 202.9, 147.2, 141.3,139.0, 135.3, 133.4, 132.6, 130.8,

129.5, 128.7, 128.6, 128.4 (2), 127.9, 127.6, 127.3, 127.2,126.8, 126.7, 125.0, 124.9, 116.3, 112.9, 71.4, 67.7, 53.7, 52.4, 40.7, 29.1; HRMS(ESI-TOF) m/z: $[M + H]^+$ $C_{36}H_{29}NO_2$calcd. 508.2271, found, 508.2263.

Ethyl (3aS,6aR)-3-benzoyl-5-oxo-1,6,6-triphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2-carboxylate (46)



Title compound was prepared according to the general procedure using 4-aminocyclopentenone derivative **1a** (0.040g, 0.12 mmol, 1.0 equiv), ethyl 4-oxo-4-phenylbut-2-ynoate **2k** (0.030g, 0.14 mmol,1.2 equiv) in presence of HFIP. The crude was then concentrated and purified by flash silica-gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as semi-solid (green) in 82% (0.051 g) yield; R_f 0.3 (EtOAc : Hexane 2:8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (m, 3H), 7.36 – 7.29 (m, 7H), 7.09 (m, 3H), 7.03 (m, 2H), 6.99 – 6.92 (m, 3H), 6.57 – 6.45 (m, 2H), 5.66 (d, J = 10.2 Hz, 1H), 4.65 (td, J = 10.3, 4.0 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.26 – 3.16 (m, 1H), 3.02 (dd, J = 19.5, 10.4 Hz, 1H), 2.65 (dd, J = 19.5, 3.9 Hz, 1H), 0.70 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 214.8, 191.5, 161.5, 152.1, 142.1, 140.6, 140.4, 139.0, 131.3, 131.0, 129.0, 128.8, 128.3, 128.2, 128.0, 127.9, 127.8, 127.1, 126.0, 124.5, 120.6, 77.2, 67.1, 61.8, 41.8, 41.6, 13.3; **HRMS** (ESI-TOF) m/z: [M+H]+ $C_{35}H_{30}NO_4$ calcd. 528.2169, found, 528.2171.

12. Crystallographic Data

Compound 3:

Crystal structures of **3** was obtained using a Bruker D8 Quest equipped with a micro-focus source for generating Mo Kα radiation (λ = 0.71073 Å) and an Apex II CCD Detector. Data were recorded at 298K. Integration and scaling of the recorded data were performed by SAINT and SADABS program respectively. Molecular structures were solved by direct methods using SHELXT-2018 and refined by full-matrix least-squares on F using SHELXL-2018/3 version. All non-hydrogen atoms in the compounds were refined anisotropically and hydrogen atoms were placed at calculated positions using riding models.

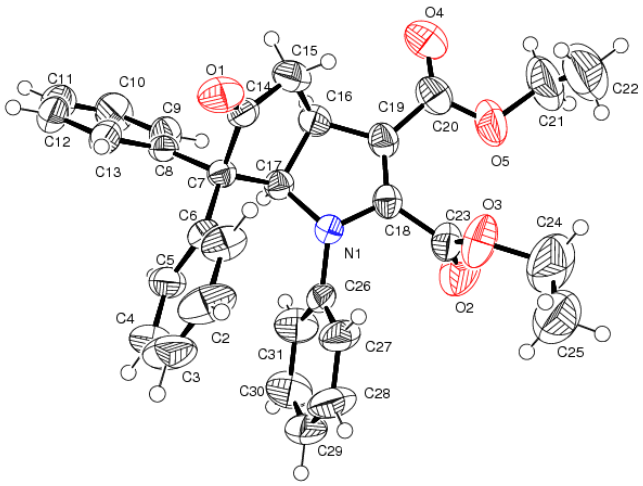


Figure S3. ORTEP diagram of 3 (CCDC No 2331633): Atoms are shown with 30% probability of thermal ellipsoids

Table S1. Crystal data and structure refinement for compound **3**

Identification code	SP-1162	
Empirical formula	C31 H29 N O5	
Formula weight	495.55	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.8447(8) Å	α= 101.529(3)°.
	b = 11.1980(8) Å	β= 90.637(3)°.
	c = 12.0881(10) Å	γ = 113.153(3)°.
Volume	1315.93(18) $Å^3$	
Z	2	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	524	
Crystal size	0.268 x 0.134 x 0.078 mm^3	
Theta range for data collection	3.457 to 25.498°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	42149	
Independent reflections	4884 [R(int) = 0.0930]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5683	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4884 / 51 / 353	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0681, wR2 = 0.1330	
R indices (all data)	R1 = 0.1094, wR2 = 0.1519	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.285 and -0.197 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for compound **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1785(3)	1593(3)	742(3)	59(1)
C(2)	2220(4)	823(3)	-78(3)	82(1)
C(3)	3402(4)	1405(4)	-531(3)	89(1)
C(4)	4163(4)	2737(4)	-175(3)	75(1)
C(5)	3725(3)	3503(3)	622(2)	54(1)
C(6)	2536(2)	2946(2)	1098(2)	40(1)
C(7)	2125(2)	3825(2)	2021(2)	36(1)
C(8)	2289(2)	5132(2)	1677(2)	39(1)
C(9)	2921(3)	6383(3)	2371(3)	55(1)
C(10)	3001(4)	7506(3)	2005(3)	72(1)
C(11)	2445(4)	7395(4)	947(3)	75(1)
C(12)	1805(3)	6163(4)	250(3)	67(1)
C(13)	1724(3)	5042(3)	608(2)	53(1)
C(14)	618(3)	3229(3)	2228(2)	44(1)
C(15)	478(3)	3690(4)	3445(3)	79(1)
C(16)	1858(3)	4237(3)	4102(2)	53(1)
C(17)	2861(2)	4114(2)	3218(2)	41(1)
C(18)	2773(3)	2783(2)	4490(2)	44(1)
C(19)	2008(3)	3425(3)	4908(2)	50(1)
C(20)	1315(3)	3336(3)	5931(3)	64(1)
C(21)	1077(5)	2548(5)	7658(3)	115(2)
C(22)	111(5)	1264(6)	7586(5)	140(2)
C(26)	4296(2)	2739(3)	3012(2)	44(1)
C(27)	4107(3)	1461(3)	2557(3)	65(1)
C(28)	5154(3)	1178(3)	2118(4)	83(1)
C(29)	6395(3)	2171(4)	2139(3)	73(1)
C(30)	6584(3)	3446(4)	2597(3)	78(1)
C(31)	5548(3)	3748(3)	3042(3)	66(1)
N(1)	3182(2)	3010(2)	3452(2)	44(1)
O(1)	-300(2)	2555(2)	1505(2)	65(1)

O(4)	505(3)	3805(3)	6161(2)	92(1)
O(5)	1699(3)	2702(3)	6604(2)	92(1)
C(23)	3310(3)	2006(3)	5089(3)	58(1)
O(2)	4386(3)	2508(3)	5624(2)	99(1)
O(3)	2472(3)	756(2)	4932(2)	87(1)
C(24)	2640(20)	-74(14)	5726(12)	134(5)
C(25)	2797(16)	-1175(13)	5012(8)	116(4)
C(24')	3215(16)	53(18)	5450(20)	92(5)
C(25')	2030(20)	-1150(30)	5540(30)	203(13)

Table S3. Bond lengths [Å] and angles [°] for Compound **3**

C(1)-C(6)	1.380(4)
C(1)-C(2)	1.392(4)
C(1)-H(1)	0.9300
C(2)-C(3)	1.368(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.363(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.375(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.382(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.526(3)
C(7)-C(8)	1.545(3)
C(7)-C(14)	1.548(3)
C(7)-C(17)	1.555(3)
C(8)-C(9)	1.378(4)
C(8)-C(13)	1.392(4)
C(9)-C(10)	1.387(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.369(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.366(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.379(4)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-O(1)	1.204(3)
C(14)-C(15)	1.488(4)
C(15)-C(16)	1.518(4)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(19)	1.507(4)
C(16)-C(17)	1.558(3)
C(16)-H(16)	0.9800

C(17)-N(1)	1.485(3)
C(17)-H(17)	0.9800
C(18)-C(19)	1.338(4)
C(18)-N(1)	1.375(3)
C(18)-C(23)	1.505(4)
C(19)-C(20)	1.454(4)
C(20)-O(4)	1.197(4)
C(20)-O(5)	1.340(4)
C(21)-C(22)	1.392(6)
C(21)-O(5)	1.457(4)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(26)-C(27)	1.359(4)
C(26)-C(31)	1.378(4)
C(26)-N(1)	1.439(3)
C(27)-C(28)	1.378(4)
C(27)-H(27)	0.9300
C(28)-C(29)	1.364(4)
C(28)-H(28)	0.9300
C(29)-C(30)	1.355(5)
C(29)-H(29)	0.9300
C(30)-C(31)	1.380(4)
C(30)-H(30)	0.9300
C(31)-H(31)	0.9300
C(23)-O(2)	1.190(3)
C(23)-O(3)	1.308(4)
O(3)-C(24)	1.518(10)
O(3)-C(24')	1.533(11)
C(24)-C(25)	1.426(14)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600

C(25)-H(25C)	0.9600
C(24')-C(25')	1.476(18)
C(24')-H(24C)	0.9700
C(24')-H(24D)	0.9700
C(25')-H(25D)	0.9600
C(25')-H(25E)	0.9600
C(25')-H(25F)	0.9600

C(6)-C(1)-C(2)	120.4(3)
C(6)-C(1)-H(1)	119.8
C(2)-C(1)-H(1)	119.8
C(3)-C(2)-C(1)	120.0(3)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.2(3)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	119.9(3)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	121.4(3)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(1)-C(6)-C(5)	118.1(2)
C(1)-C(6)-C(7)	122.4(2)
C(5)-C(6)-C(7)	119.5(2)
C(6)-C(7)-C(8)	110.77(19)
C(6)-C(7)-C(14)	114.7(2)
C(8)-C(7)-C(14)	102.57(17)
C(6)-C(7)-C(17)	114.01(18)
C(8)-C(7)-C(17)	111.06(19)
C(14)-C(7)-C(17)	102.95(19)
C(9)-C(8)-C(13)	117.6(2)
C(9)-C(8)-C(7)	124.4(2)
C(13)-C(8)-C(7)	118.0(2)
C(8)-C(9)-C(10)	120.8(3)

C(8)-C(9)-H(9)	119.6
C(10)-C(9)-H(9)	119.6
C(11)-C(10)-C(9)	120.7(3)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	119.4(3)
C(12)-C(11)-H(11)	120.3
C(10)-C(11)-H(11)	120.3
C(11)-C(12)-C(13)	120.2(3)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(12)-C(13)-C(8)	121.3(3)
C(12)-C(13)-H(13)	119.3
C(8)-C(13)-H(13)	119.3
O(1)-C(14)-C(15)	125.4(3)
O(1)-C(14)-C(7)	125.2(2)
C(15)-C(14)-C(7)	109.3(2)
C(14)-C(15)-C(16)	108.2(2)
C(14)-C(15)-H(15A)	110.1
C(16)-C(15)-H(15A)	110.1
C(14)-C(15)-H(15B)	110.1
C(16)-C(15)-H(15B)	110.1
H(15A)-C(15)-H(15B)	108.4
C(19)-C(16)-C(15)	114.9(3)
C(19)-C(16)-C(17)	102.8(2)
C(15)-C(16)-C(17)	106.6(2)
C(19)-C(16)-H(16)	110.7
C(15)-C(16)-H(16)	110.7
C(17)-C(16)-H(16)	110.7
N(1)-C(17)-C(7)	114.56(19)
N(1)-C(17)-C(16)	103.50(19)
C(7)-C(17)-C(16)	107.20(19)
N(1)-C(17)-H(17)	110.4
C(7)-C(17)-H(17)	110.4
C(16)-C(17)-H(17)	110.4
C(19)-C(18)-N(1)	113.1(2)

C(19)-C(18)-C(23)	126.7(2)
N(1)-C(18)-C(23)	119.8(2)
C(18)-C(19)-C(20)	128.3(3)
C(18)-C(19)-C(16)	109.7(2)
C(20)-C(19)-C(16)	122.0(3)
O(4)-C(20)-O(5)	123.4(3)
O(4)-C(20)-C(19)	123.6(3)
O(5)-C(20)-C(19)	113.0(3)
C(22)-C(21)-O(5)	112.3(4)
C(22)-C(21)-H(21A)	109.2
O(5)-C(21)-H(21A)	109.2
C(22)-C(21)-H(21B)	109.2
O(5)-C(21)-H(21B)	109.2
H(21A)-C(21)-H(21B)	107.9
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(27)-C(26)-C(31)	119.3(2)
C(27)-C(26)-N(1)	119.2(2)
C(31)-C(26)-N(1)	121.4(2)
C(26)-C(27)-C(28)	120.3(3)
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-H(27)	119.8
C(29)-C(28)-C(27)	120.7(3)
C(29)-C(28)-H(28)	119.6
C(27)-C(28)-H(28)	119.6
C(30)-C(29)-C(28)	118.9(3)
C(30)-C(29)-H(29)	120.5
C(28)-C(29)-H(29)	120.5
C(29)-C(30)-C(31)	121.2(3)
C(29)-C(30)-H(30)	119.4
C(31)-C(30)-H(30)	119.4
C(26)-C(31)-C(30)	119.5(3)

C(26)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(18)-N(1)-C(26)	121.4(2)
C(18)-N(1)-C(17)	108.65(19)
C(26)-N(1)-C(17)	122.8(2)
C(20)-O(5)-C(21)	118.3(3)
O(2)-C(23)-O(3)	126.1(3)
O(2)-C(23)-C(18)	121.9(3)
O(3)-C(23)-C(18)	112.0(3)
C(23)-O(3)-C(24)	119.0(8)
C(23)-O(3)-C(24')	106.4(7)
C(25)-C(24)-O(3)	105.4(11)
C(25)-C(24)-H(24A)	110.7
O(3)-C(24)-H(24A)	110.7
C(25)-C(24)-H(24B)	110.7
O(3)-C(24)-H(24B)	110.7
H(24A)-C(24)-H(24B)	108.8
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(25')-C(24')-O(3)	97.8(15)
C(25')-C(24')-H(24C)	112.2
O(3)-C(24')-H(24C)	112.2
C(25')-C(24')-H(24D)	112.2
O(3)-C(24')-H(24D)	112.2
H(24C)-C(24')-H(24D)	109.8
C(24')-C(25')-H(25D)	109.5
C(24')-C(25')-H(25E)	109.5
H(25D)-C(25')-H(25E)	109.5
C(24')-C(25')-H(25F)	109.5
H(25D)-C(25')-H(25F)	109.5
H(25E)-C(25')-H(25F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Compound **3**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(2)	40(2)	82(2)	2(2)	-4(2)	17(1)
C(2)	78(2)	54(2)	104(3)	-24(2)	-20(2)	37(2)
C(3)	101(3)	99(3)	82(3)	-14(2)	3(2)	73(3)
C(4)	76(2)	92(3)	75(2)	17(2)	28(2)	53(2)
C(5)	52(2)	54(2)	62(2)	14(1)	16(1)	27(1)
C(6)	38(1)	39(1)	44(2)	8(1)	-2(1)	19(1)
C(7)	34(1)	34(1)	41(1)	9(1)	5(1)	14(1)
C(8)	35(1)	41(1)	47(2)	14(1)	10(1)	19(1)
C(9)	70(2)	41(2)	56(2)	13(1)	9(2)	22(1)
C(10)	95(3)	42(2)	85(3)	20(2)	25(2)	30(2)
C(11)	88(2)	67(2)	101(3)	51(2)	38(2)	48(2)
C(12)	64(2)	83(2)	73(2)	43(2)	14(2)	39(2)
C(13)	51(2)	56(2)	58(2)	21(1)	2(1)	24(1)
C(14)	37(2)	44(2)	58(2)	20(1)	7(1)	19(1)
C(15)	61(2)	134(3)	67(2)	39(2)	24(2)	57(2)
C(16)	64(2)	59(2)	47(2)	12(1)	14(1)	34(2)
C(17)	40(1)	38(1)	44(2)	11(1)	5(1)	15(1)
C(18)	43(2)	40(1)	42(2)	11(1)	1(1)	10(1)
C(19)	59(2)	52(2)	38(2)	10(1)	7(1)	22(1)
C(20)	74(2)	66(2)	45(2)	4(2)	11(2)	25(2)
C(21)	155(4)	139(4)	61(3)	44(3)	44(3)	58(4)
C(22)	120(4)	161(5)	140(5)	82(4)	50(3)	34(4)
C(26)	38(1)	53(2)	48(2)	20(1)	4(1)	23(1)
C(27)	45(2)	51(2)	109(3)	34(2)	24(2)	24(1)
C(28)	64(2)	62(2)	144(4)	36(2)	34(2)	41(2)
C(29)	51(2)	92(3)	94(3)	31(2)	21(2)	42(2)
C(30)	37(2)	85(3)	99(3)	17(2)	10(2)	13(2)
C(31)	44(2)	62(2)	80(2)	2(2)	1(2)	14(2)
N(1)	43(1)	50(1)	45(1)	19(1)	9(1)	23(1)
O(1)	35(1)	64(1)	86(2)	10(1)	-1(1)	13(1)
O(4)	109(2)	120(2)	68(2)	21(1)	36(1)	66(2)

O(5)	130(2)	113(2)	56(2)	42(1)	36(1)	61(2)
C(23)	64(2)	62(2)	53(2)	23(2)	4(2)	24(2)
O(2)	78(2)	119(2)	97(2)	39(2)	-31(2)	30(2)
O(3)	112(2)	57(1)	93(2)	34(1)	-6(2)	28(1)
C(24)	145(12)	82(7)	188(12)	67(7)	25(8)	42(9)
C(25)	161(11)	107(8)	107(7)	29(5)	11(6)	77(8)
C(24')	105(11)	76(9)	114(11)	67(8)	-1(8)	36(8)
C(25')	190(20)	160(19)	270(30)	150(20)	5(19)	29(17)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound **3**.

	x	y	z	U(eq)
H(1)	983	1194	1053	71
H(2)	1707	-88	-317	99
H(3)	3688	891	-1084	106
H(4)	4977	3127	-470	90
H(5)	4239	4415	845	65
H(9)	3299	6475	3094	66
H(10)	3436	8343	2483	87
H(11)	2503	8152	705	90
H(12)	1423	6079	-469	80
H(13)	1283	4209	125	63
H(15A)	-146	2953	3733	95
H(15B)	132	4377	3529	95
H(16)	2121	5168	4496	64
H(17)	3677	4941	3346	49
H(21A)	1770	2758	8266	138
H(21B)	659	3176	7844	138
H(22A)	-271	1208	8296	210
H(22B)	-587	1059	6994	210
H(22C)	524	640	7417	210
H(27)	3267	773	2541	78
H(28)	5012	300	1805	99
H(29)	7099	1977	1842	88
H(30)	7427	4129	2613	94
H(31)	5695	4626	3361	80
H(24A)	3429	441	6267	161
H(24B)	1854	-380	6138	161
H(25A)	2909	-1742	5468	175
H(25B)	2011	-1669	4480	175
H(25C)	3576	-853	4608	175
H(24C)	3828	-160	4952	110

H(24D)	3696	566	6186	110
H(25D)	2312	-1723	5866	304
H(25E)	1432	-888	6023	304
H(25F)	1562	-1605	4804	304

Table S6. Torsion angles [°] for Compound **3**

C(6)-C(1)-C(2)-C(3)	0.4(5)
C(1)-C(2)-C(3)-C(4)	0.6(6)
C(2)-C(3)-C(4)-C(5)	-1.6(6)
C(3)-C(4)-C(5)-C(6)	1.7(5)
C(2)-C(1)-C(6)-C(5)	-0.3(4)
C(2)-C(1)-C(6)-C(7)	-178.0(3)
C(4)-C(5)-C(6)-C(1)	-0.7(4)
C(4)-C(5)-C(6)-C(7)	177.0(3)
C(1)-C(6)-C(7)-C(8)	-135.8(2)
C(5)-C(6)-C(7)-C(8)	46.6(3)
C(1)-C(6)-C(7)-C(14)	-20.3(3)
C(5)-C(6)-C(7)-C(14)	162.1(2)
C(1)-C(6)-C(7)-C(17)	98.1(3)
C(5)-C(6)-C(7)-C(17)	-79.6(3)
C(6)-C(7)-C(8)-C(9)	-132.0(3)
C(14)-C(7)-C(8)-C(9)	105.1(3)
C(17)-C(7)-C(8)-C(9)	-4.3(3)
C(6)-C(7)-C(8)-C(13)	50.1(3)
C(14)-C(7)-C(8)-C(13)	-72.8(3)
C(17)-C(7)-C(8)-C(13)	177.8(2)
C(13)-C(8)-C(9)-C(10)	-0.7(4)
C(7)-C(8)-C(9)-C(10)	-178.6(3)
C(8)-C(9)-C(10)-C(11)	0.4(5)
C(9)-C(10)-C(11)-C(12)	0.1(5)
C(10)-C(11)-C(12)-C(13)	-0.2(5)
C(11)-C(12)-C(13)-C(8)	-0.2(4)
C(9)-C(8)-C(13)-C(12)	0.7(4)
C(7)-C(8)-C(13)-C(12)	178.7(2)
C(6)-C(7)-C(14)-O(1)	-35.3(3)
C(8)-C(7)-C(14)-O(1)	84.9(3)
C(17)-C(7)-C(14)-O(1)	-159.7(2)
C(6)-C(7)-C(14)-C(15)	148.3(2)
C(8)-C(7)-C(14)-C(15)	-91.5(3)
C(17)-C(7)-C(14)-C(15)	23.9(3)

O(1)-C(14)-C(15)-C(16)	167.6(3)
C(7)-C(14)-C(15)-C(16)	-16.0(3)
C(14)-C(15)-C(16)-C(19)	-112.0(3)
C(14)-C(15)-C(16)-C(17)	1.1(3)
C(6)-C(7)-C(17)-N(1)	-33.2(3)
C(8)-C(7)-C(17)-N(1)	-159.22(19)
C(14)-C(7)-C(17)-N(1)	91.6(2)
C(6)-C(7)-C(17)-C(16)	-147.4(2)
C(8)-C(7)-C(17)-C(16)	86.6(2)
C(14)-C(7)-C(17)-C(16)	-22.6(2)
C(19)-C(16)-C(17)-N(1)	13.6(3)
C(15)-C(16)-C(17)-N(1)	-107.6(3)
C(19)-C(16)-C(17)-C(7)	135.0(2)
C(15)-C(16)-C(17)-C(7)	13.9(3)
N(1)-C(18)-C(19)-C(20)	174.6(3)
C(23)-C(18)-C(19)-C(20)	-12.2(5)
N(1)-C(18)-C(19)-C(16)	-1.3(3)
C(23)-C(18)-C(19)-C(16)	171.8(3)
C(15)-C(16)-C(19)-C(18)	107.2(3)
C(17)-C(16)-C(19)-C(18)	-8.2(3)
C(15)-C(16)-C(19)-C(20)	-69.1(4)
C(17)-C(16)-C(19)-C(20)	175.6(3)
C(18)-C(19)-C(20)-O(4)	-169.4(3)
C(16)-C(19)-C(20)-O(4)	6.1(5)
C(18)-C(19)-C(20)-O(5)	12.0(5)
C(16)-C(19)-C(20)-O(5)	-172.5(3)
C(31)-C(26)-C(27)-C(28)	-0.8(5)
N(1)-C(26)-C(27)-C(28)	179.2(3)
C(26)-C(27)-C(28)-C(29)	0.4(6)
C(27)-C(28)-C(29)-C(30)	-0.1(6)
C(28)-C(29)-C(30)-C(31)	0.2(6)
C(27)-C(26)-C(31)-C(30)	0.9(5)
N(1)-C(26)-C(31)-C(30)	-179.1(3)
C(29)-C(30)-C(31)-C(26)	-0.6(5)
C(19)-C(18)-N(1)-C(26)	162.0(2)
C(23)-C(18)-N(1)-C(26)	-11.6(4)

C(19)-C(18)-N(1)-C(17)	10.9(3)
C(23)-C(18)-N(1)-C(17)	-162.8(2)
C(27)-C(26)-N(1)-C(18)	77.6(3)
C(31)-C(26)-N(1)-C(18)	-102.4(3)
C(27)-C(26)-N(1)-C(17)	-135.4(3)
C(31)-C(26)-N(1)-C(17)	44.6(4)
C(7)-C(17)-N(1)-C(18)	-131.5(2)
C(16)-C(17)-N(1)-C(18)	-15.1(3)
C(7)-C(17)-N(1)-C(26)	77.9(3)
C(16)-C(17)-N(1)-C(26)	-165.7(2)
O(4)-C(20)-O(5)-C(21)	1.4(5)
C(19)-C(20)-O(5)-C(21)	180.0(3)
C(22)-C(21)-O(5)-C(20)	103.4(5)
C(19)-C(18)-C(23)-O(2)	-91.6(4)
N(1)-C(18)-C(23)-O(2)	81.1(4)
C(19)-C(18)-C(23)-O(3)	89.2(4)
N(1)-C(18)-C(23)-O(3)	-98.0(3)
O(2)-C(23)-O(3)-C(24)	18.5(9)
C(18)-C(23)-O(3)-C(24)	-162.4(8)
O(2)-C(23)-O(3)-C(24')	-6.3(11)
C(18)-C(23)-O(3)-C(24')	172.9(11)
C(23)-O(3)-C(24)-C(25)	-122.8(14)
C(23)-O(3)-C(24')-C(25')	162(2)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for Compound **3** [Å and °].

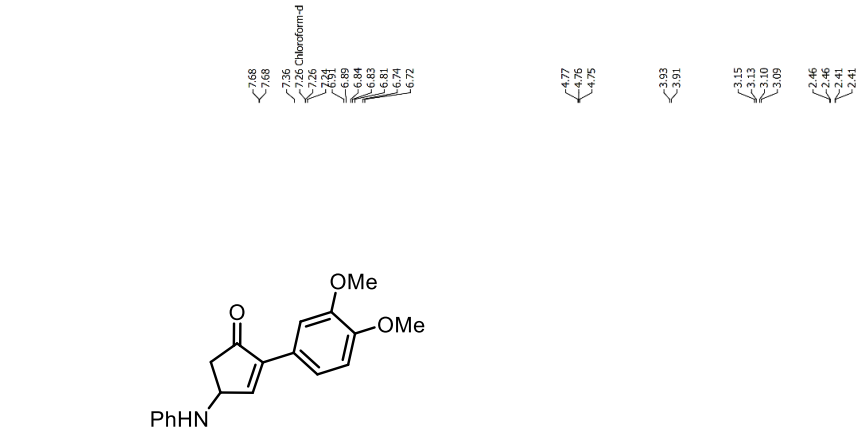
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(15)-H(15B)...O(4)#1	0.97	2.36	3.326(5)	174.3
C(25')-H(25F)...O(4)#2	0.96	2.63	3.41(3)	139.2

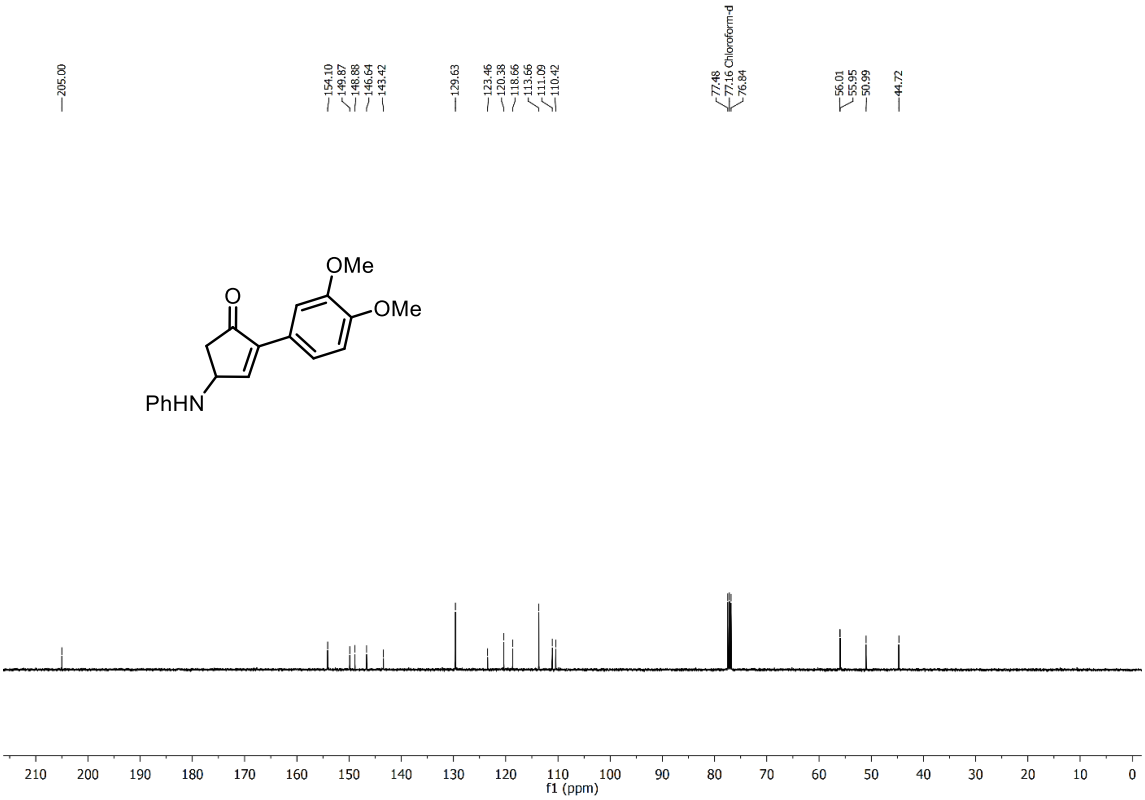
Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x,-y,-z+1

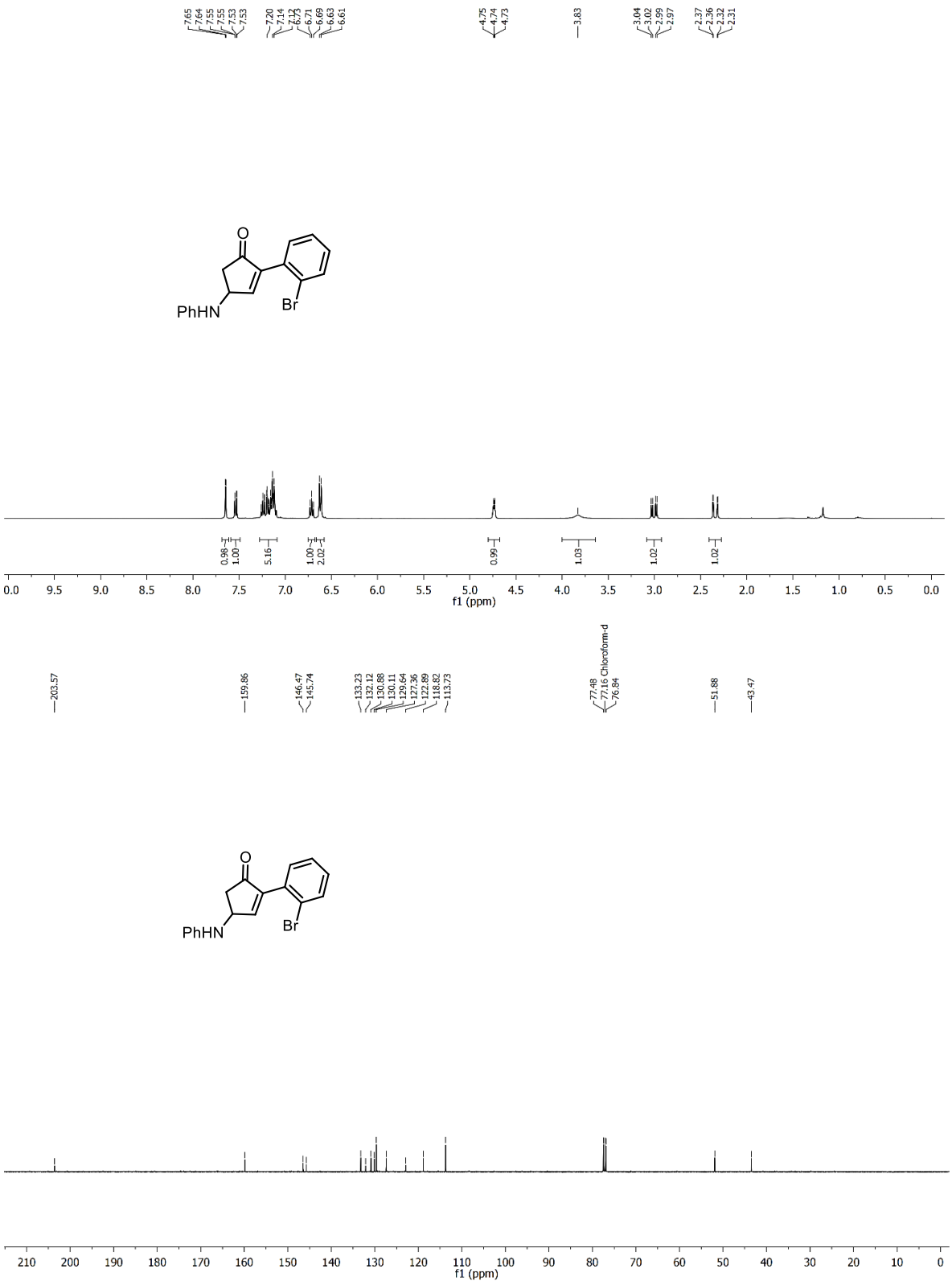
13. NMR spectra of new compound

^{1}H NMR spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1'd)***

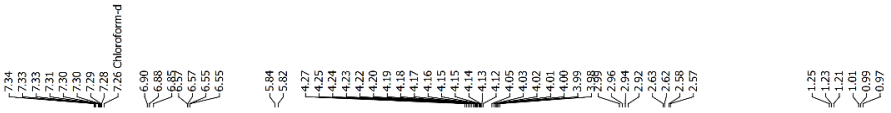


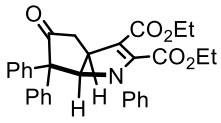


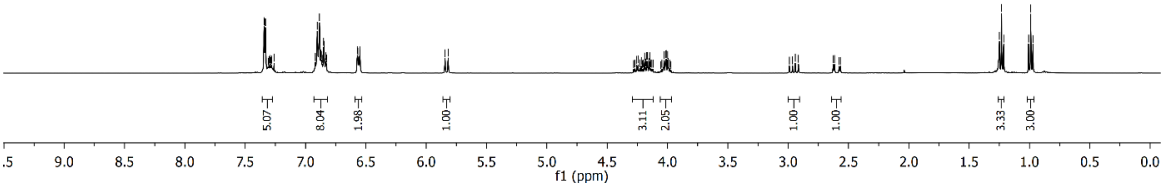
^{1}H NMR spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(1'e)***

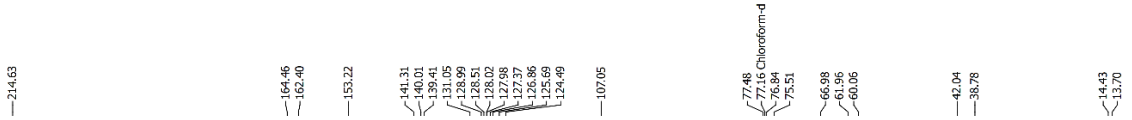


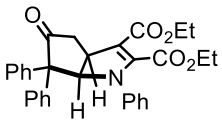
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(3)***

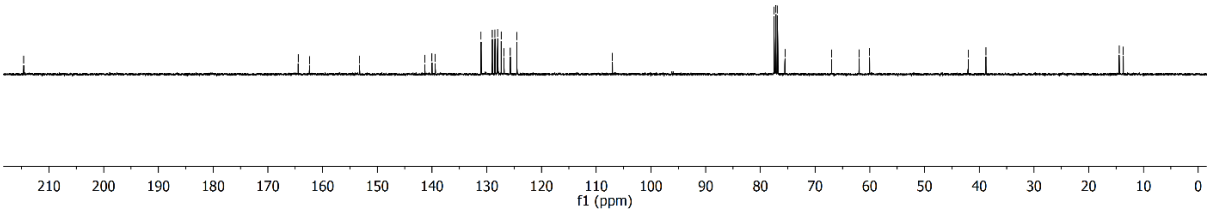




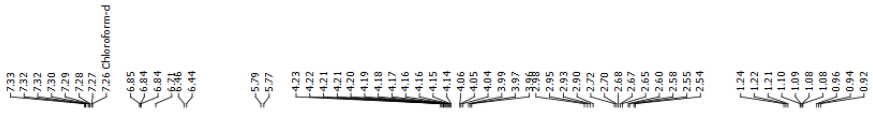


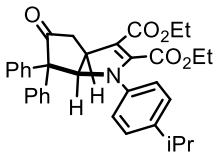


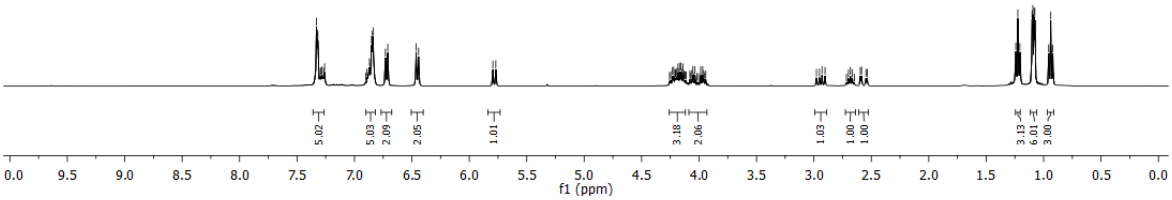


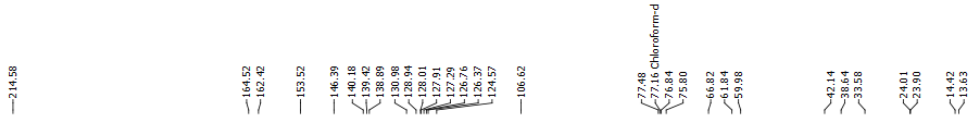


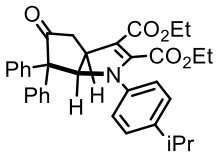
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(4)***

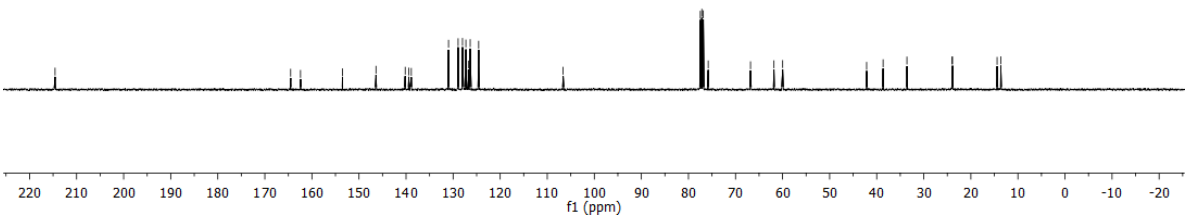




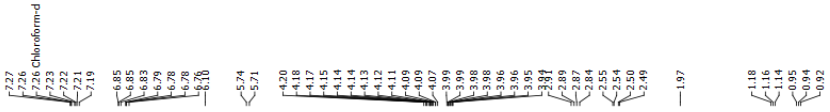


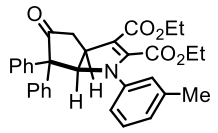


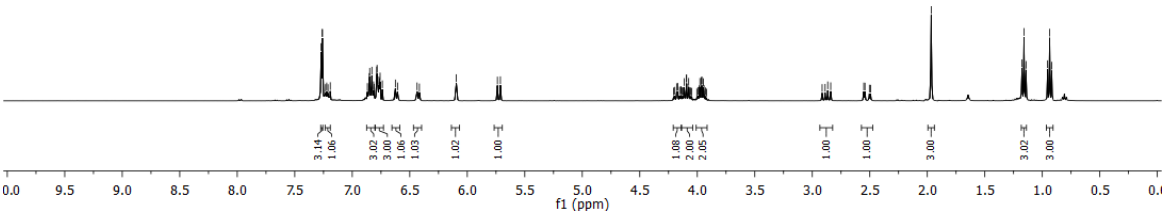


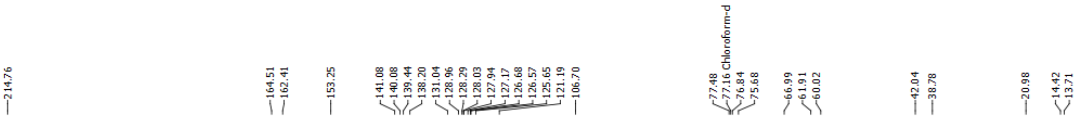


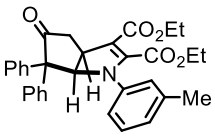
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(5)***

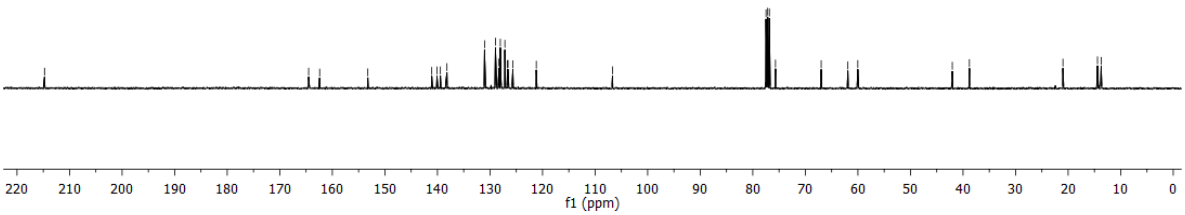




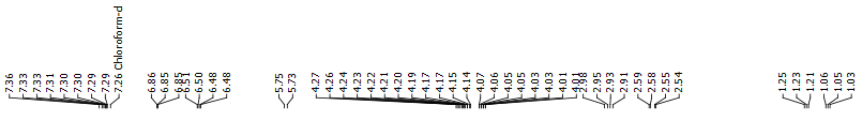


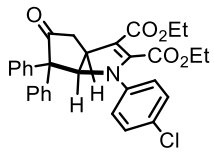


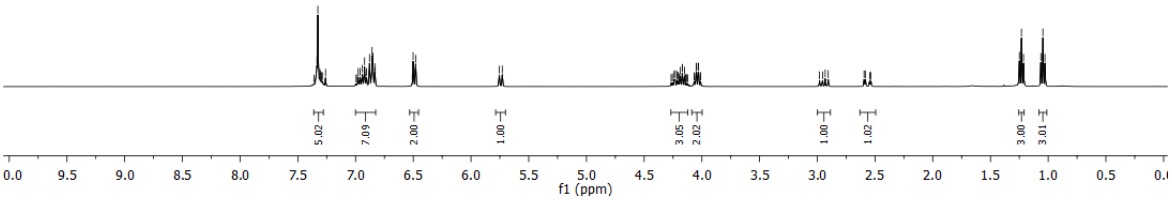


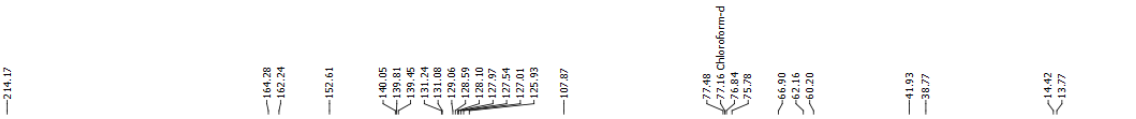


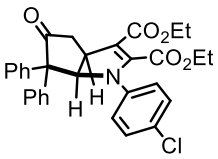
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(6)***

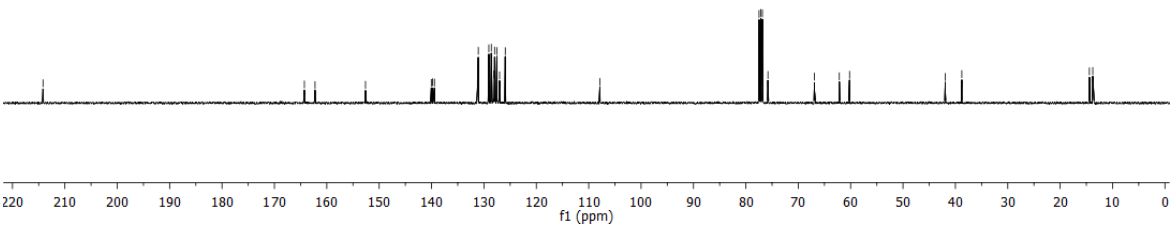




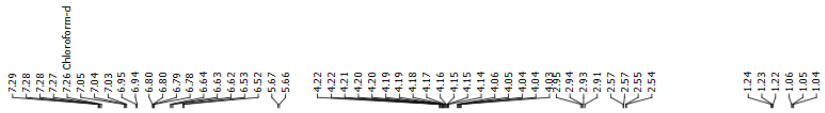


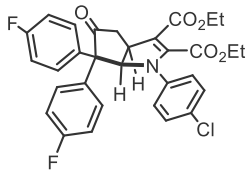


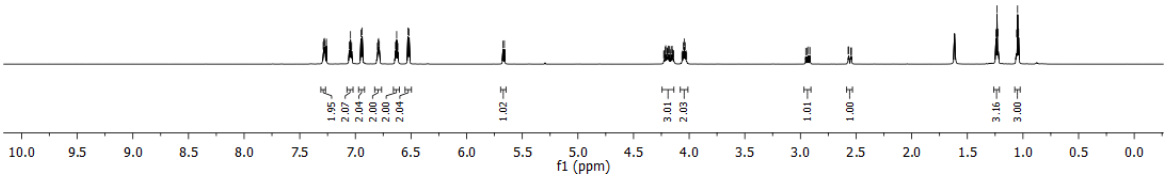


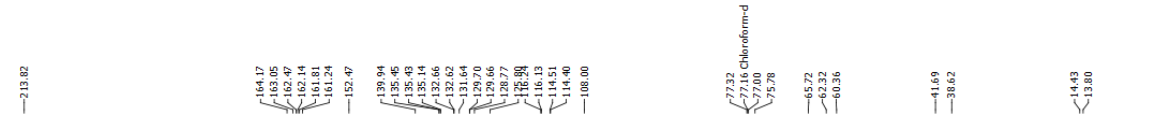


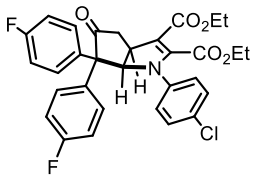
*^{1}H NMR spectra at 800MHz and ^{13}C NMR spectra at 200MHz in $CDCl_3$**(7)***



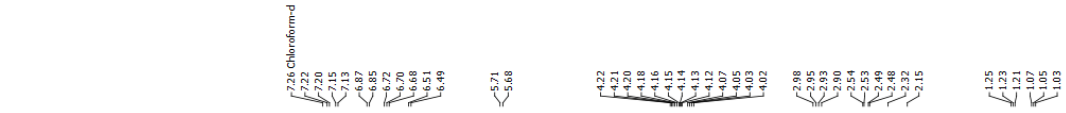


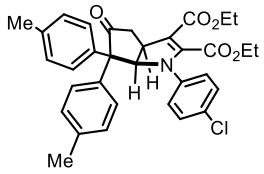


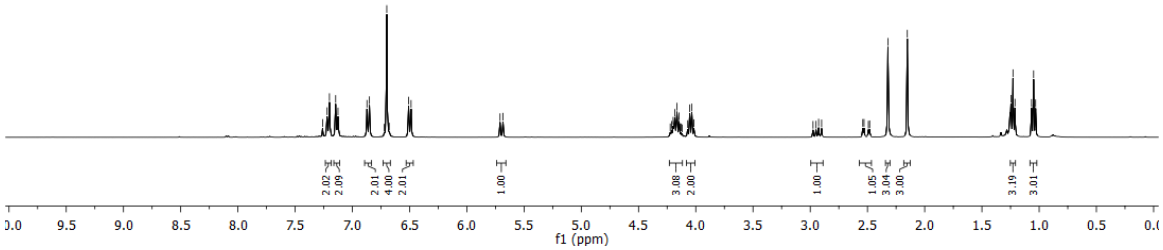


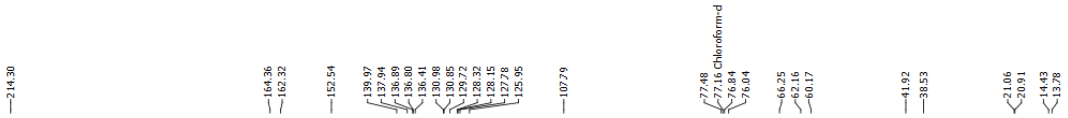


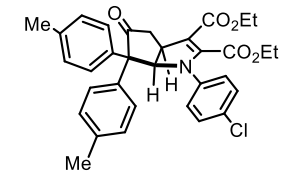
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(8)***

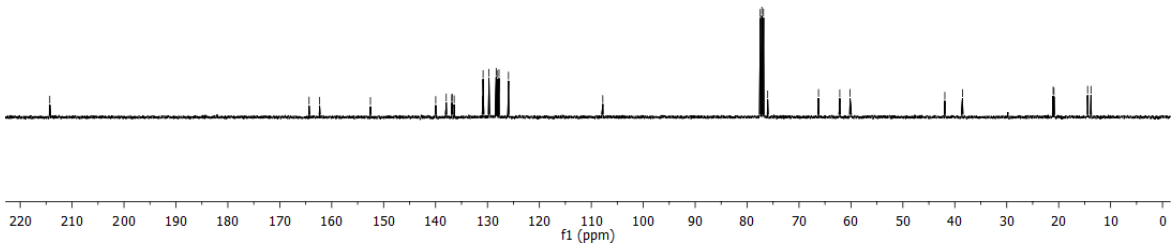




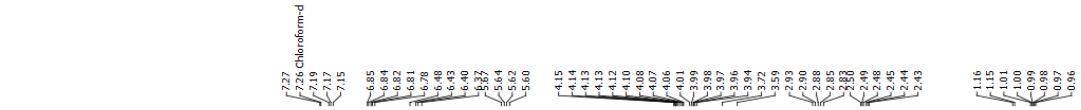


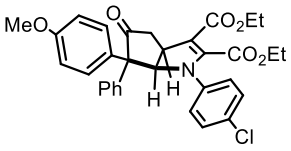


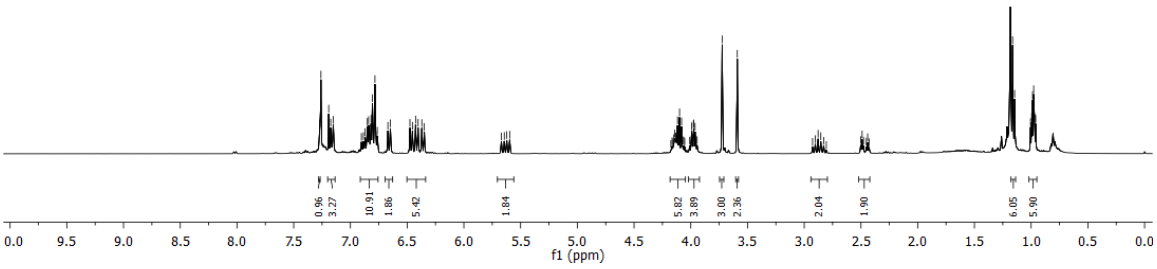


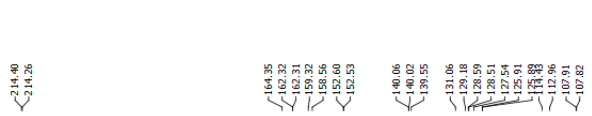


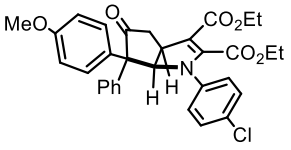
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(9)***

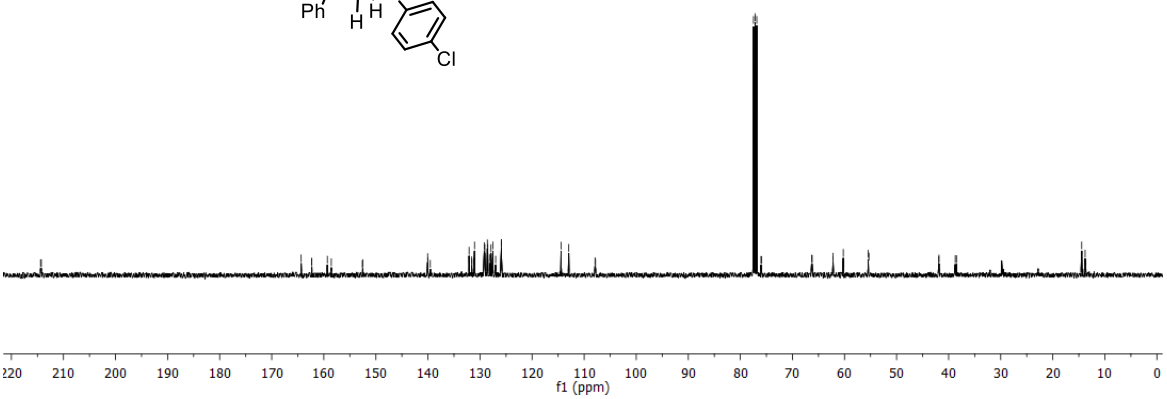




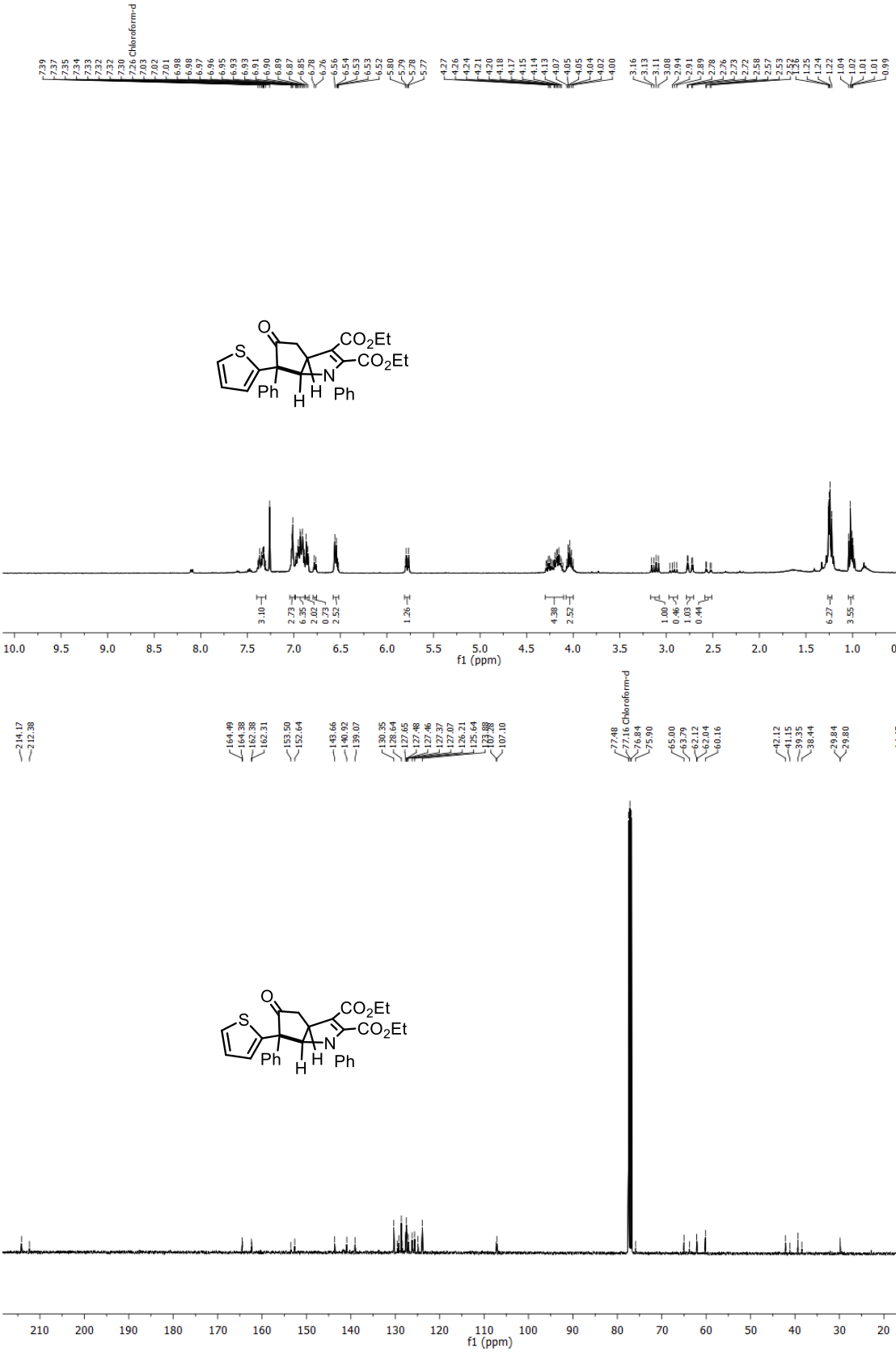




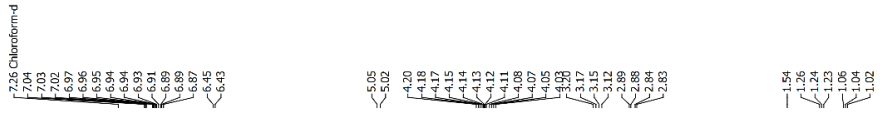


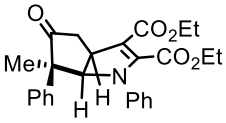


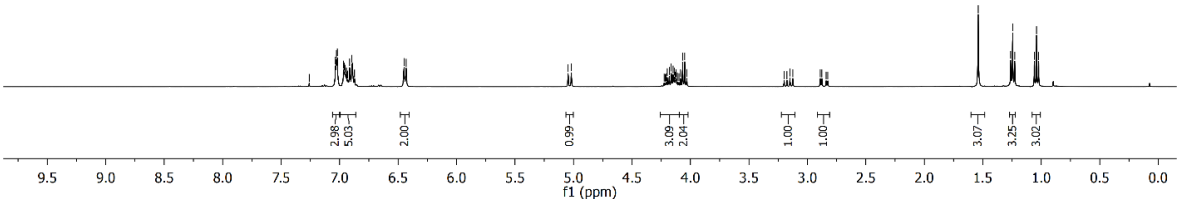
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(10)***

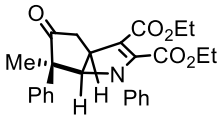


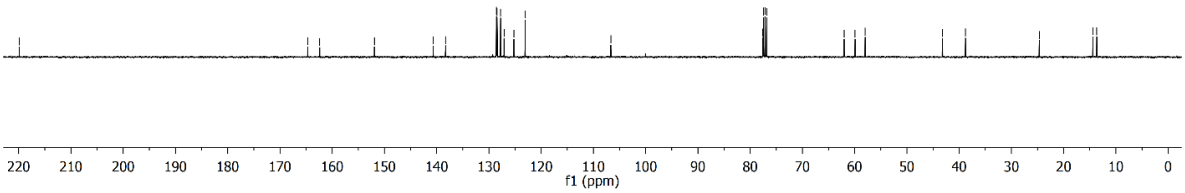
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(11)***



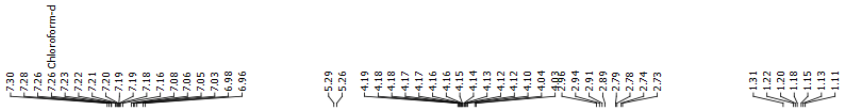


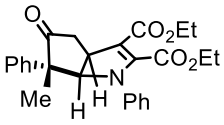


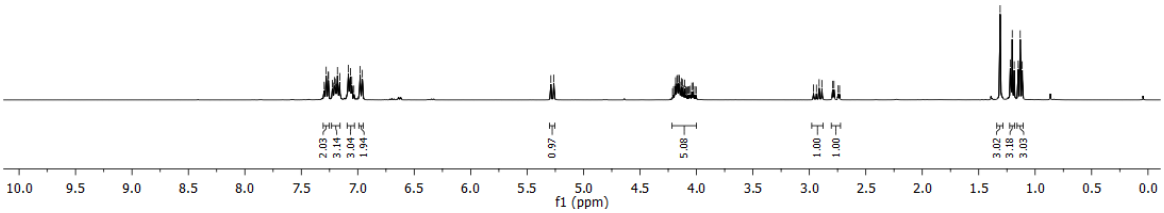


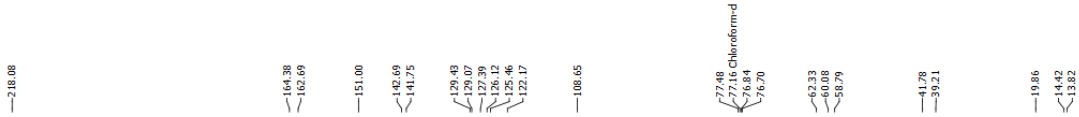


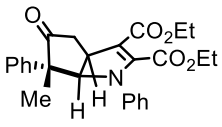
*^{1}H spectra at 400MHz and^{13}C NMR spectra at 100MHz in $CDCl_3$**(12)***

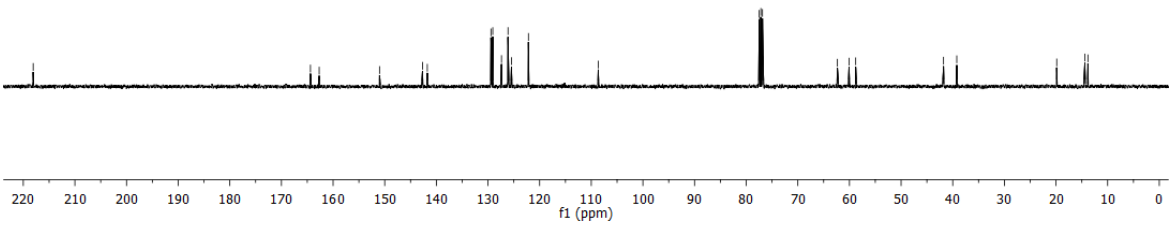




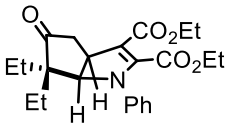


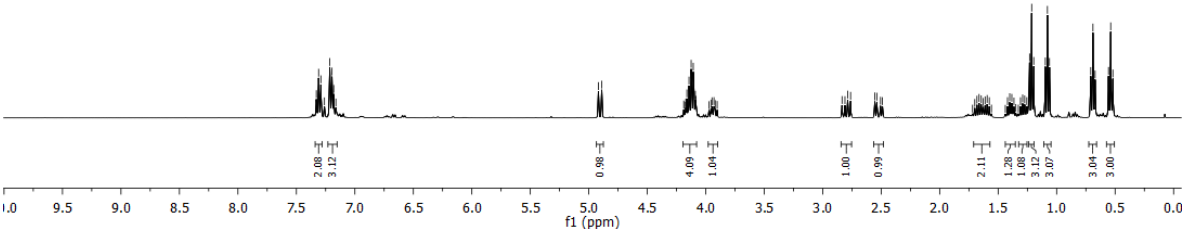


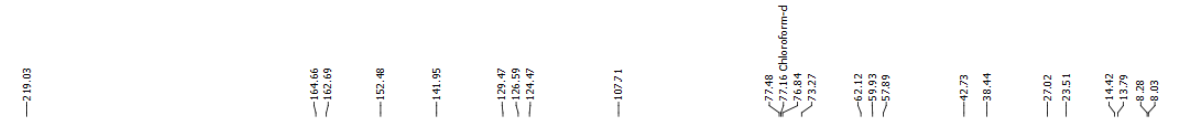


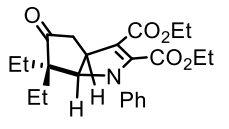


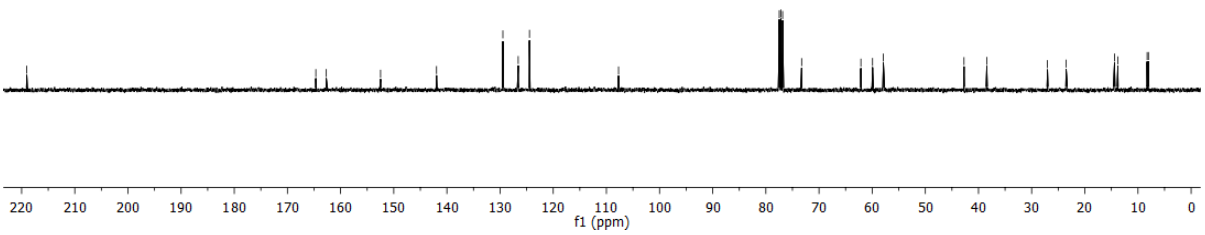
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(13)***



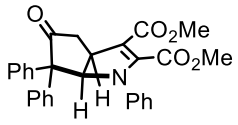


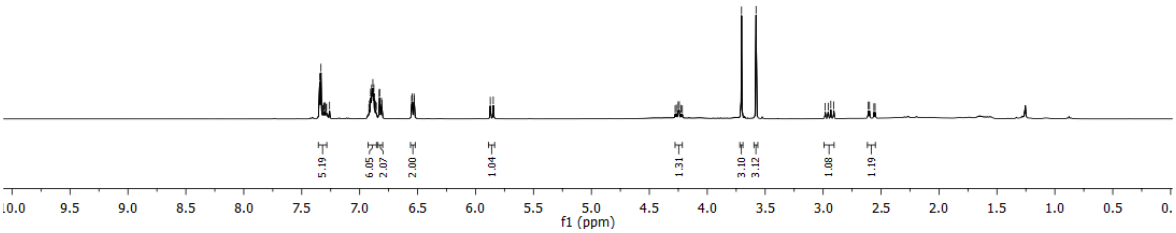


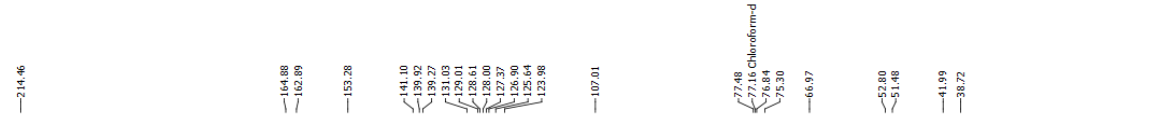


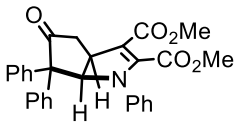


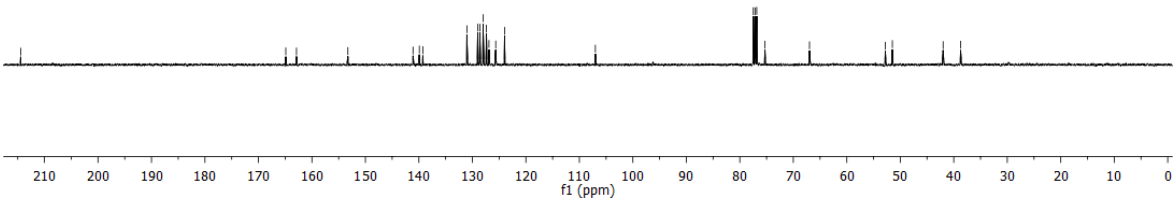
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(14)***



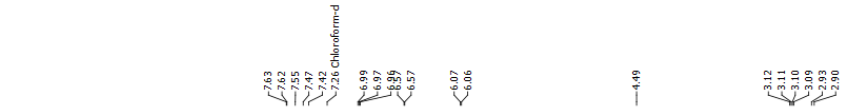


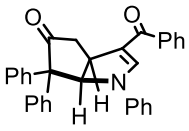


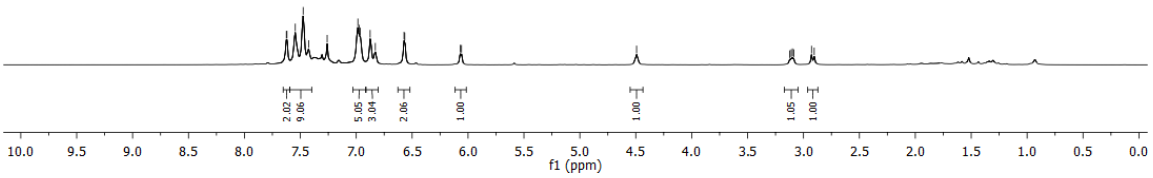


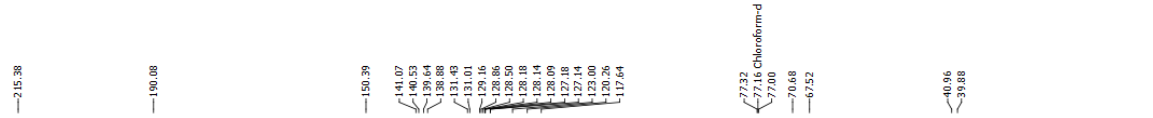


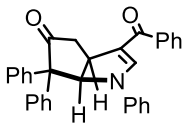
*^{1}H NMR spectra at 800MHz and ^{13}C NMR spectra at 200MHz in $CDCl_3$**(15)***

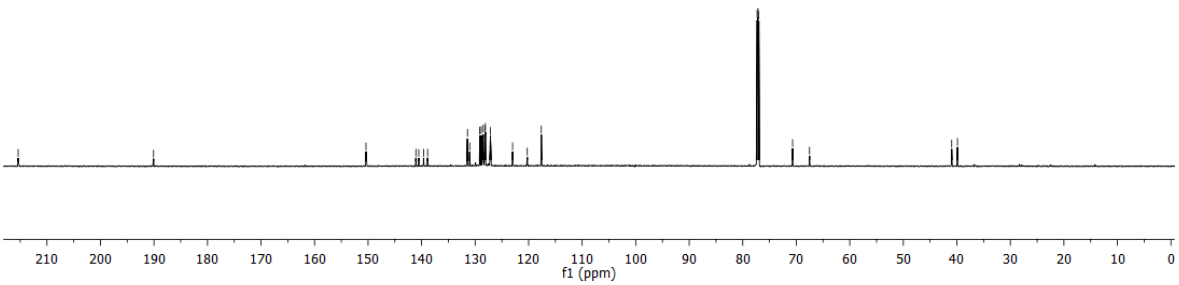




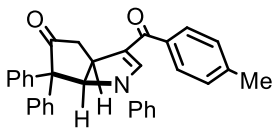


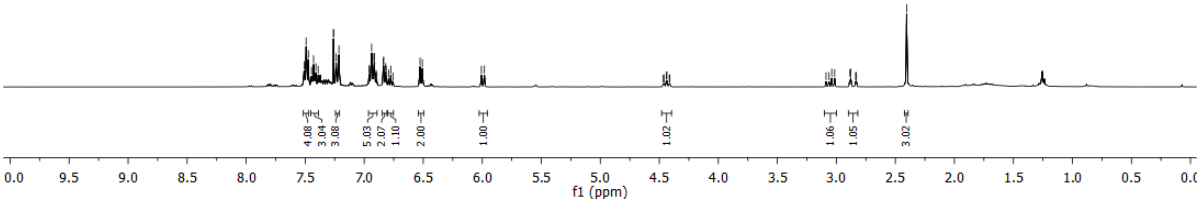


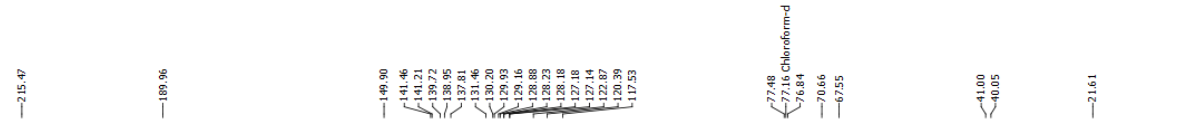


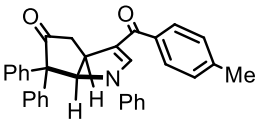


^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(16)***

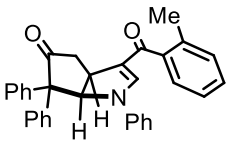


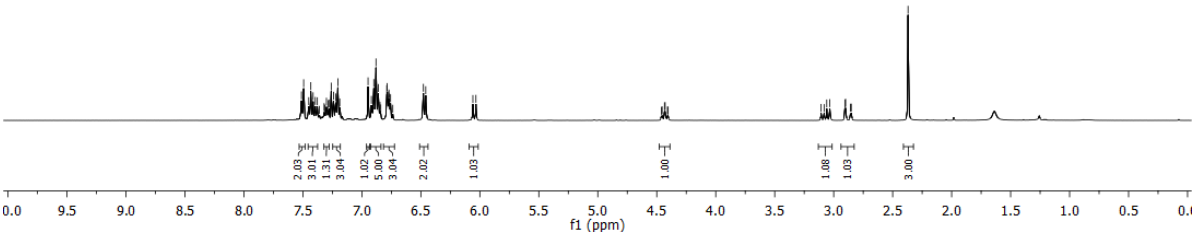


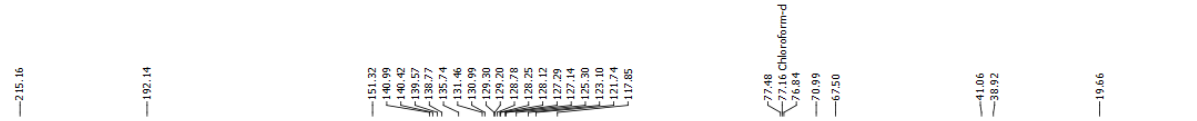


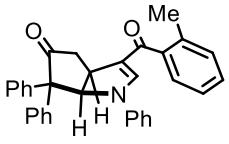


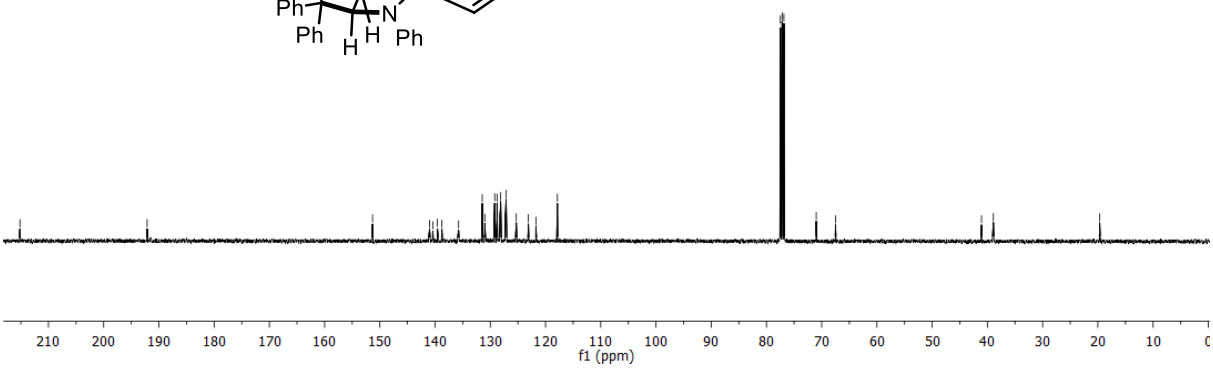
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(17)***



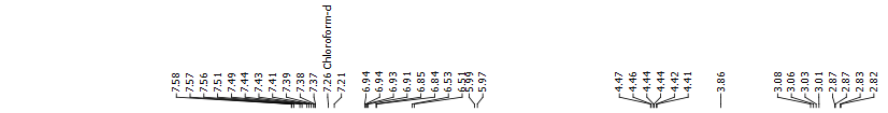


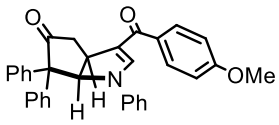


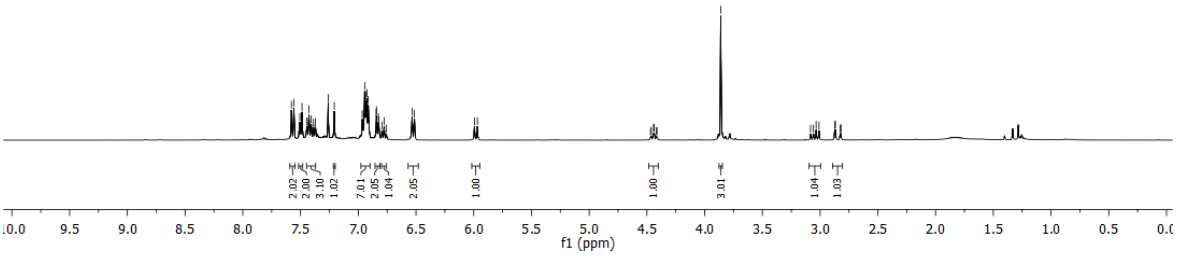


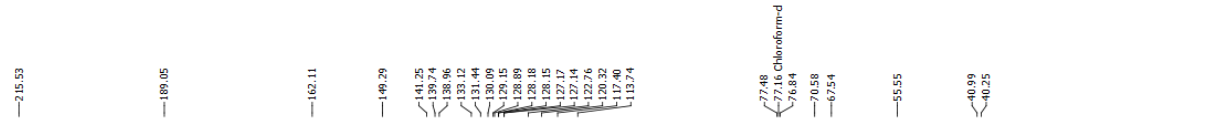


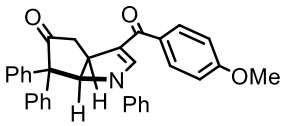
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(18)***



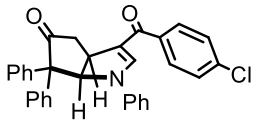


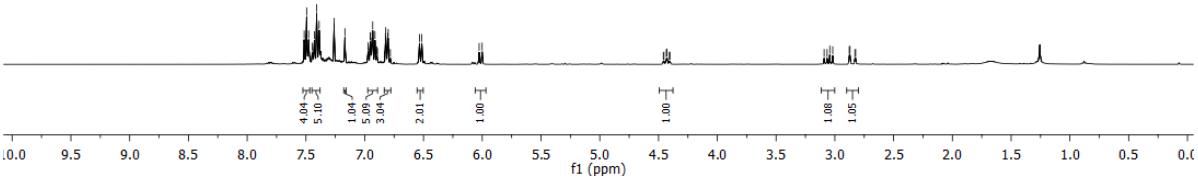


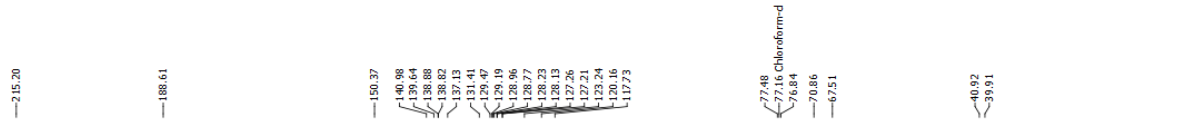


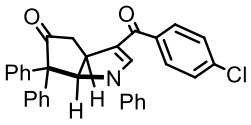


^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(19)***

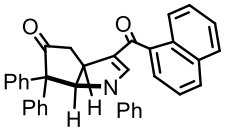


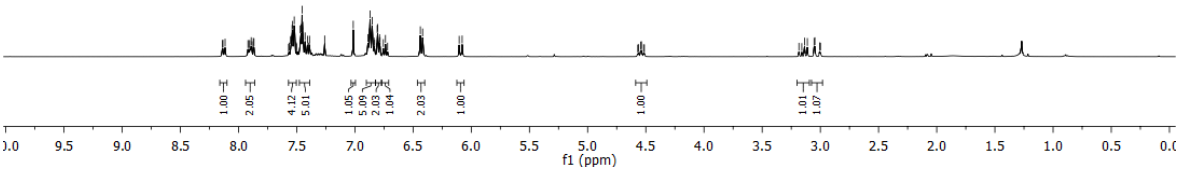


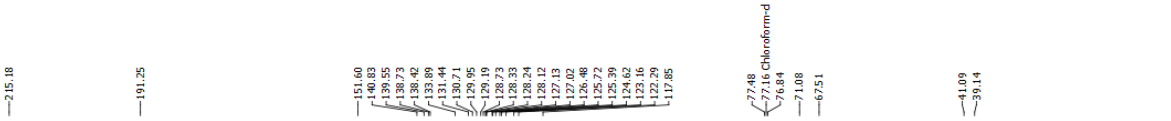


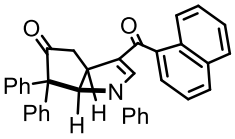


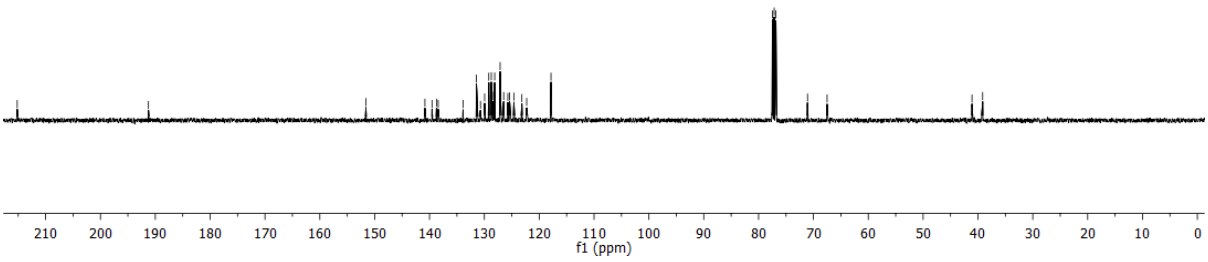
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(20)***



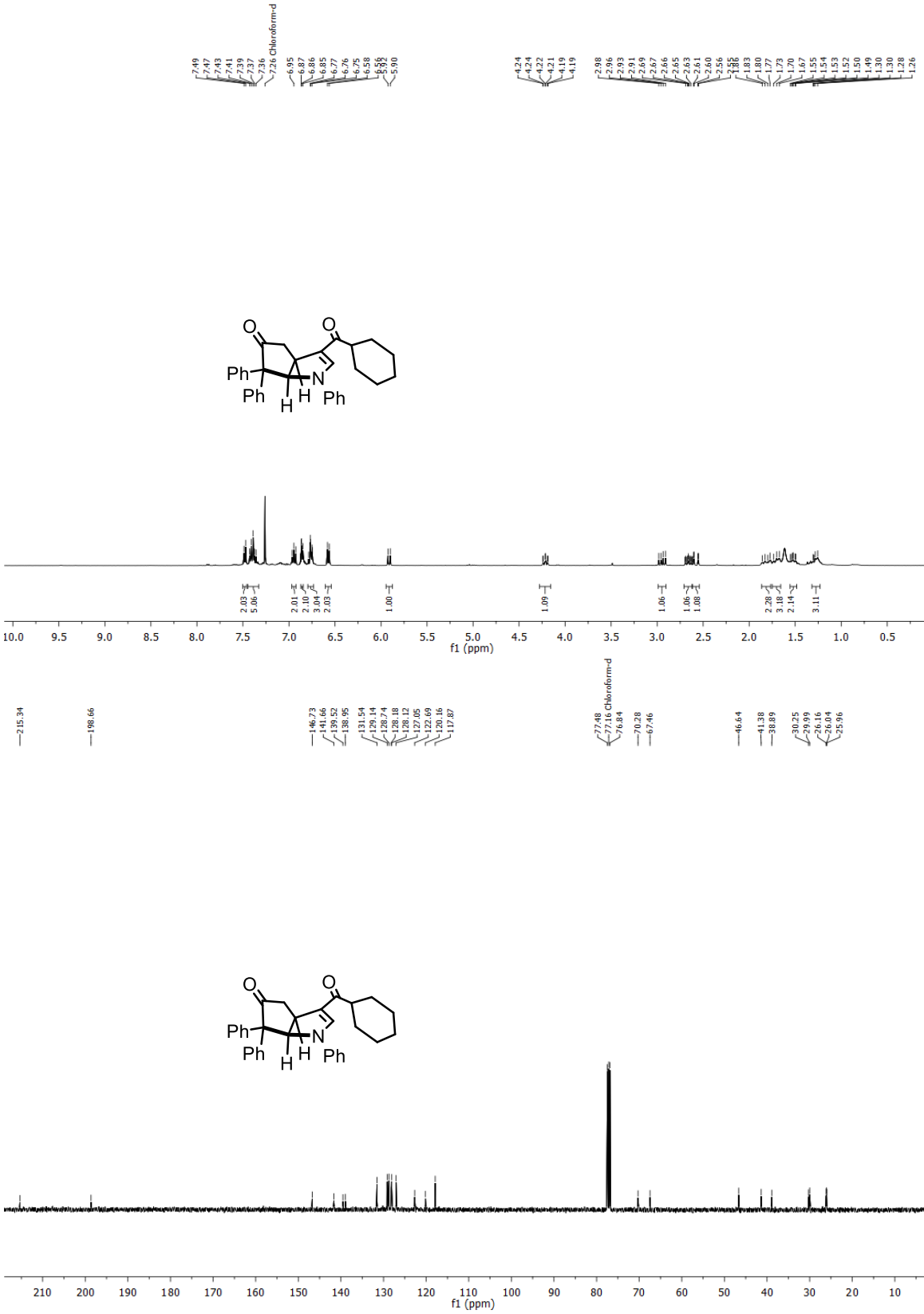




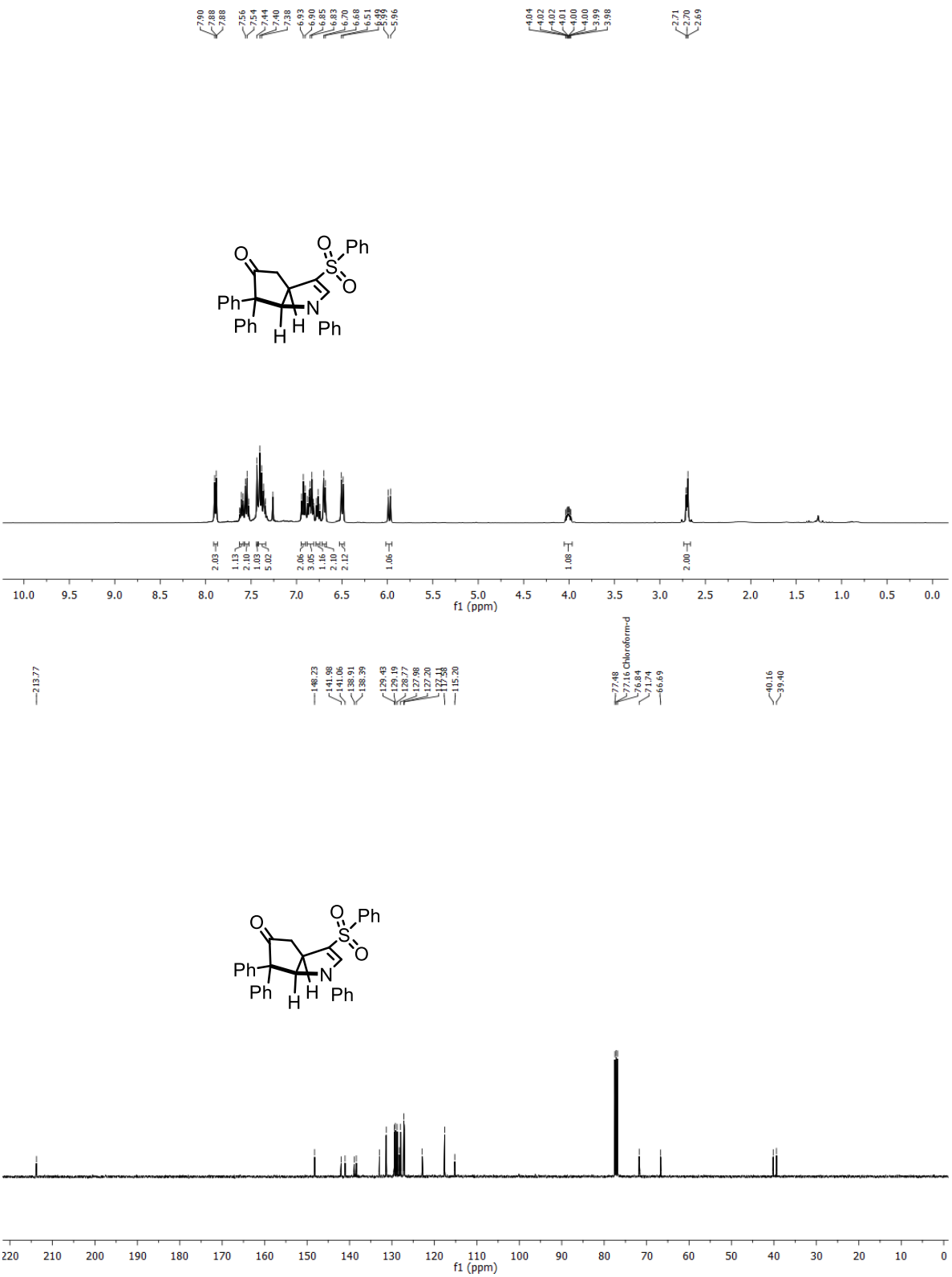




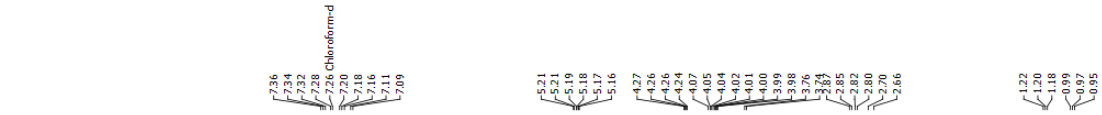
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(21)***

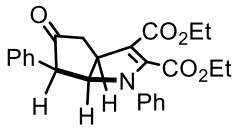


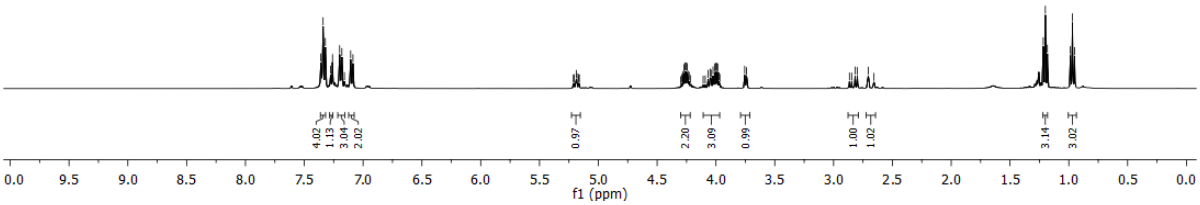
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(22)***

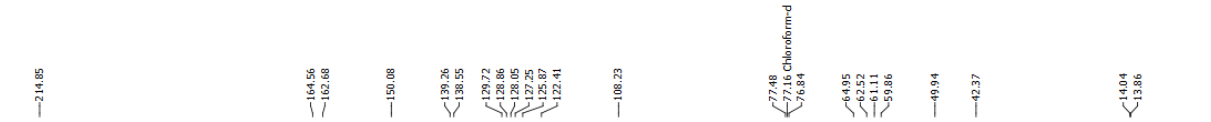


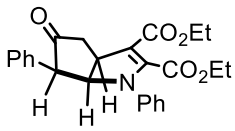
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(23)***

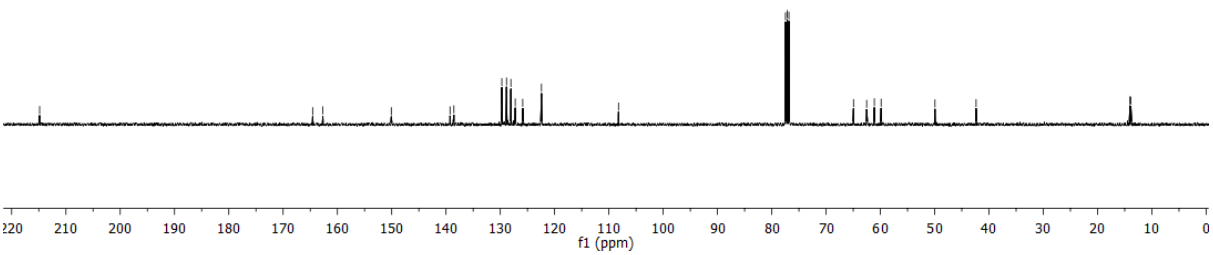




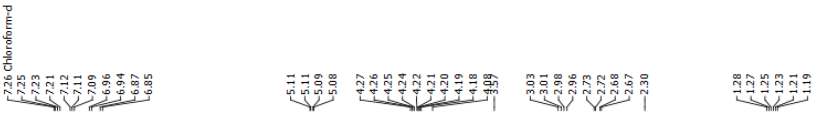


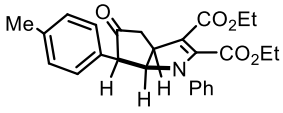


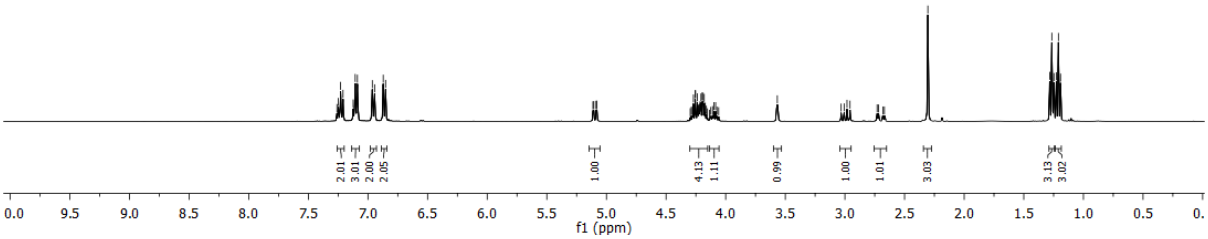


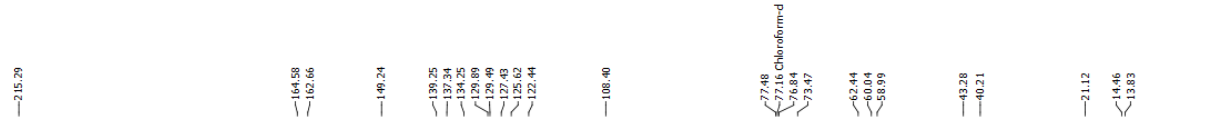


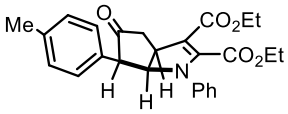
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(24)***

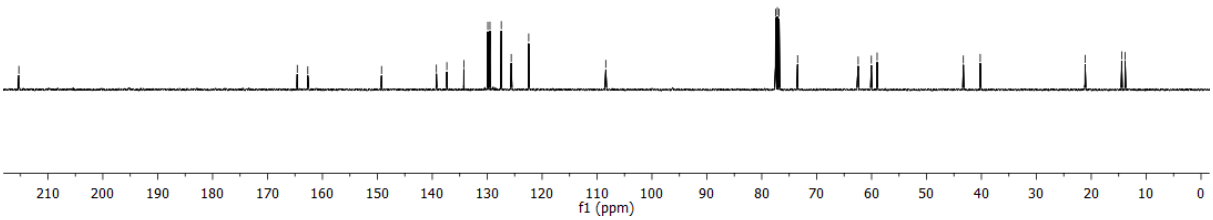




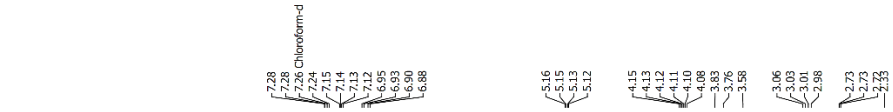


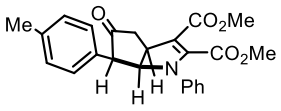


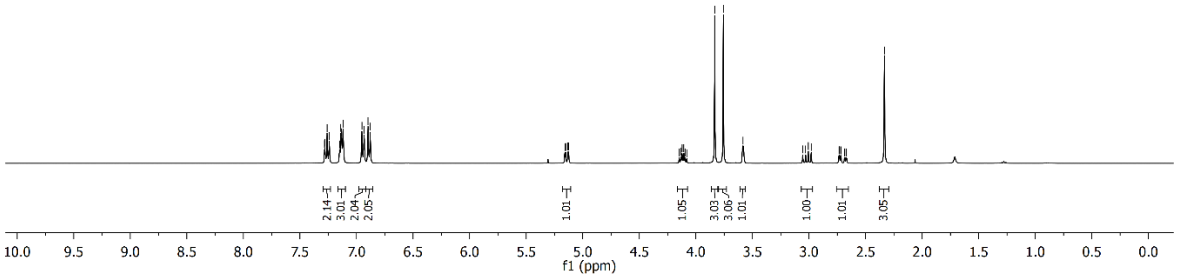


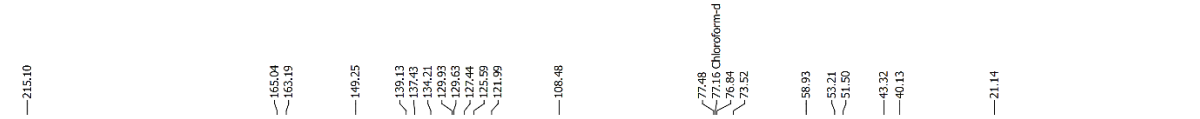


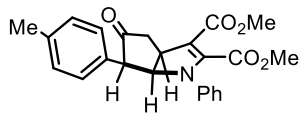
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(25)***

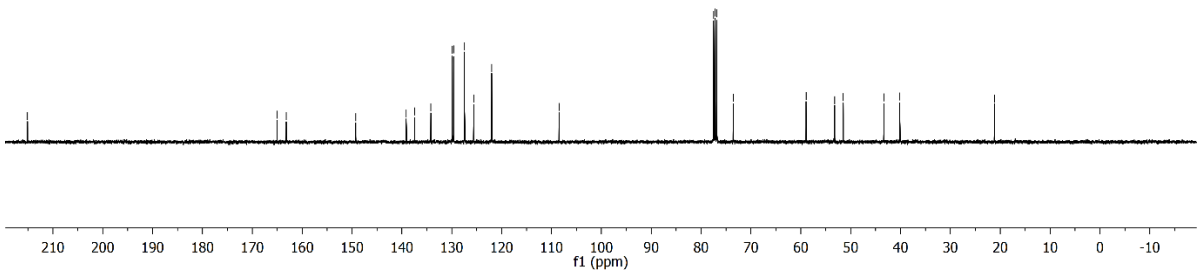




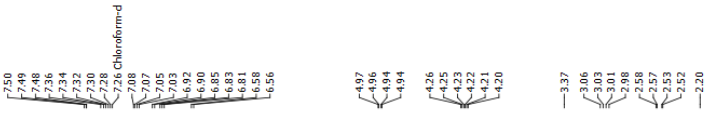


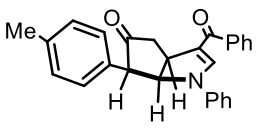


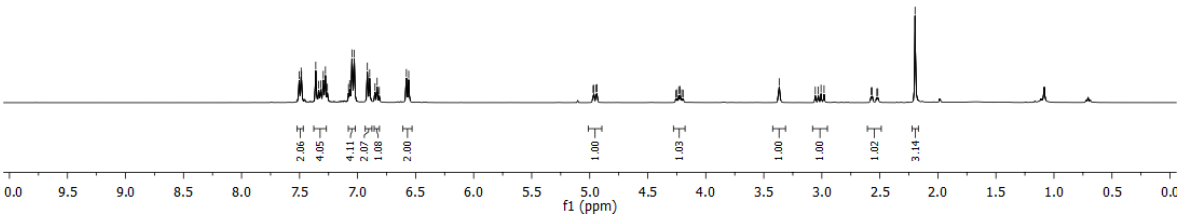


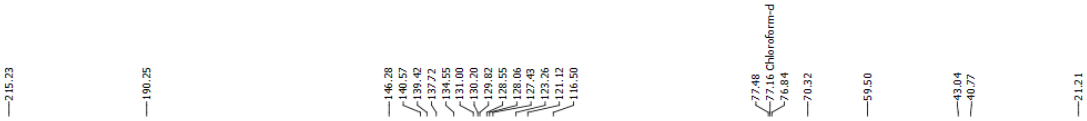


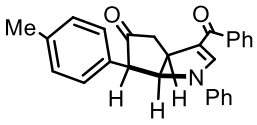
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(26)***

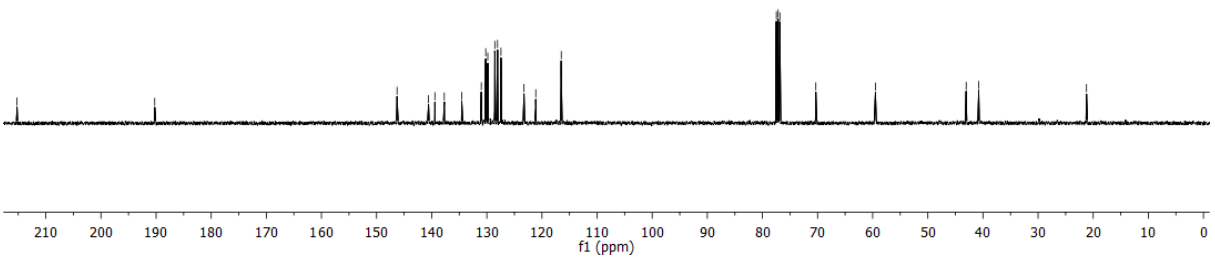




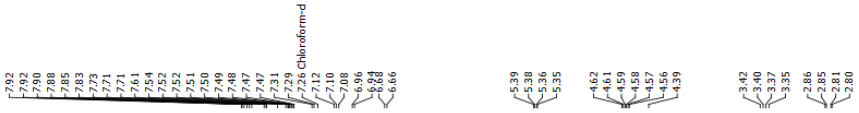


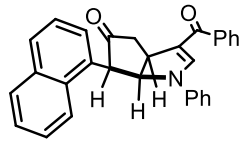


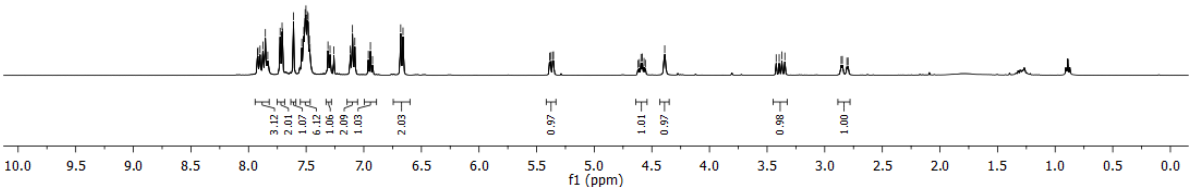


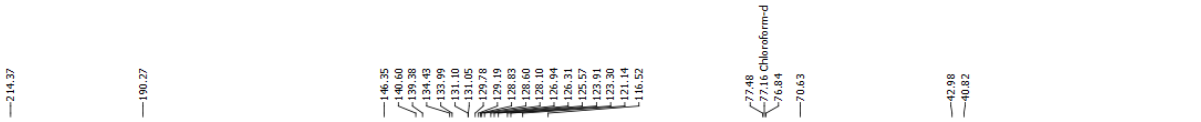


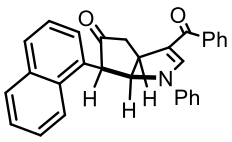
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(27)***

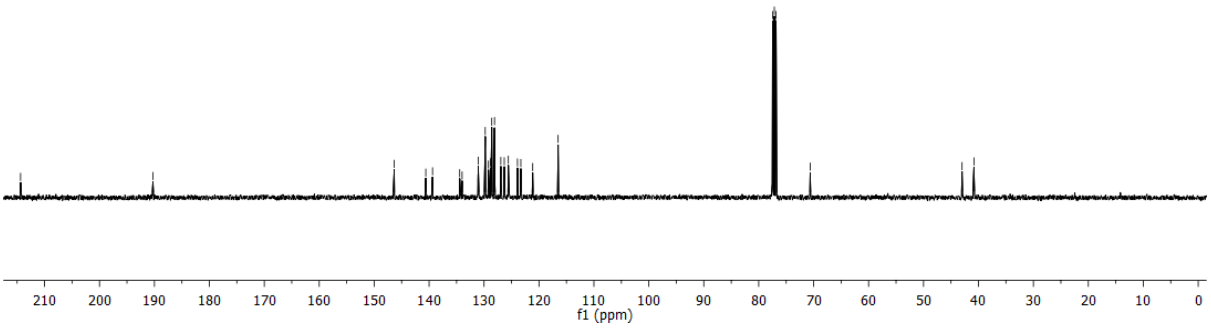




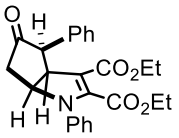


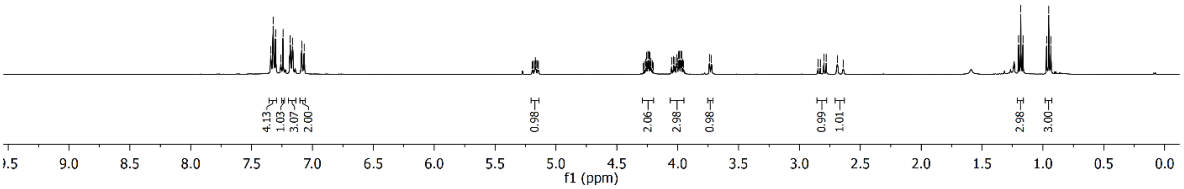


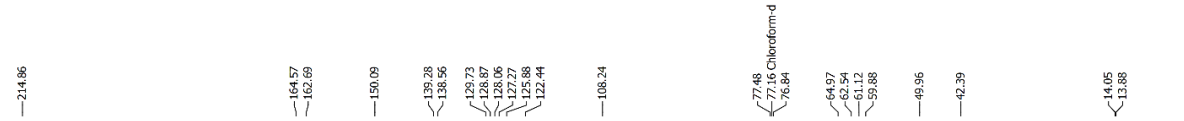


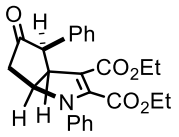


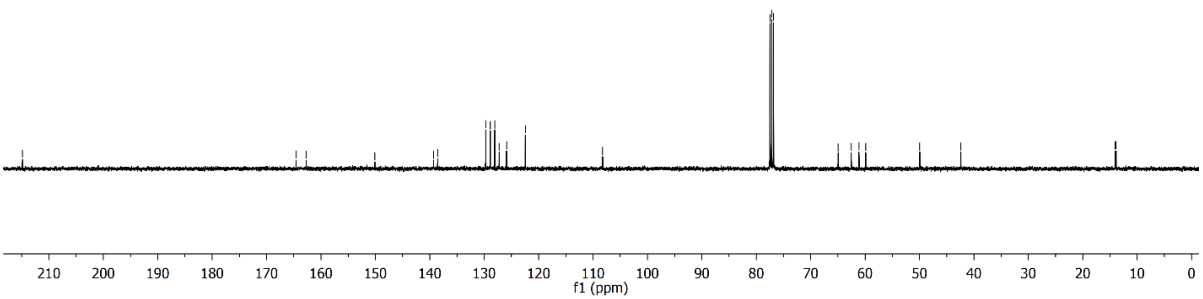
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(28)***



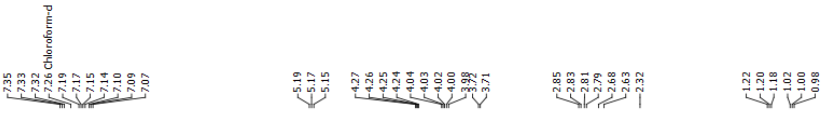


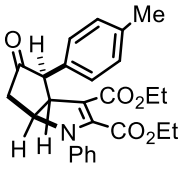


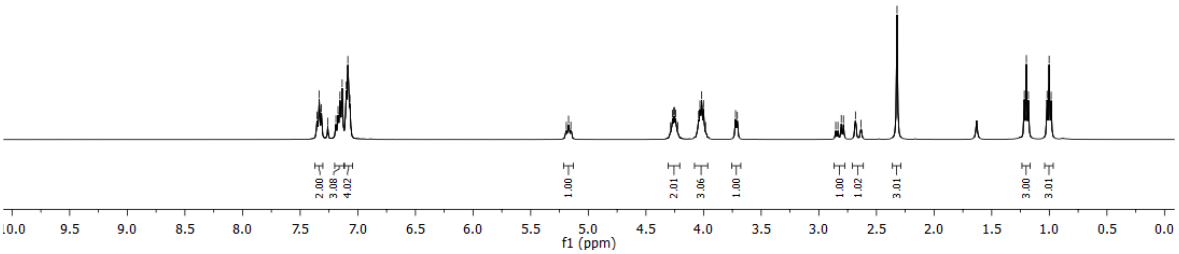


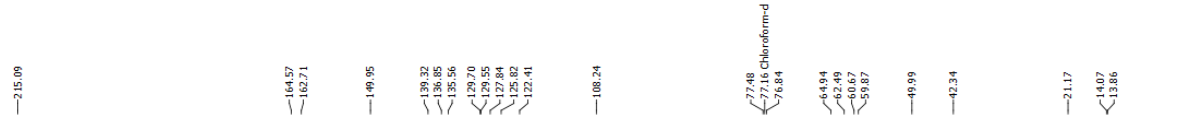


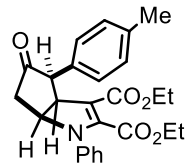
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(29)***

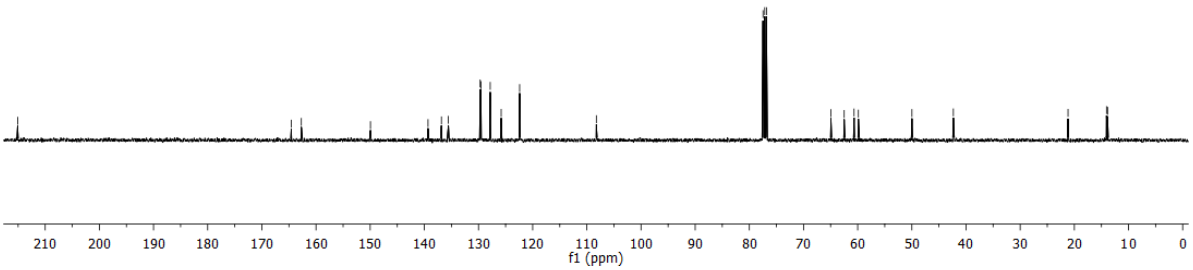




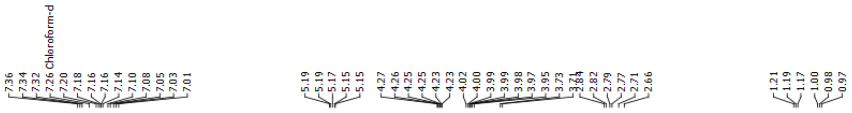


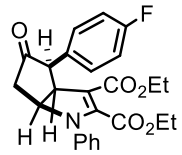


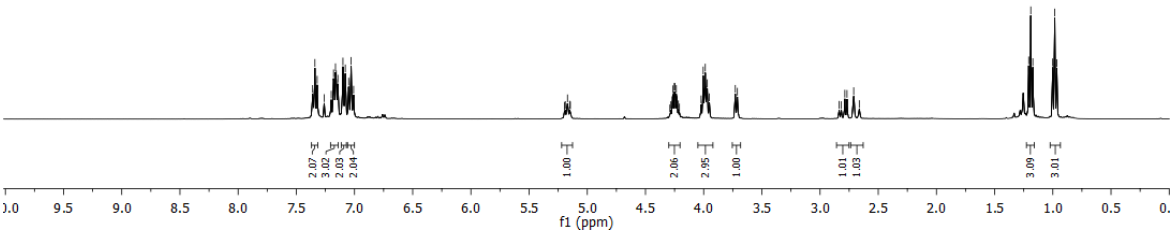


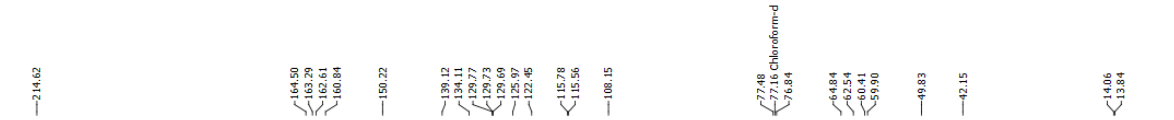


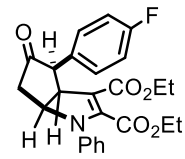
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(30)***

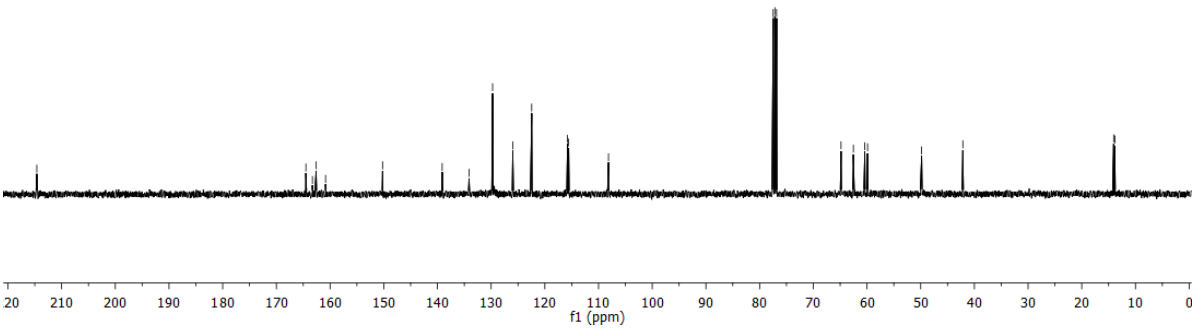




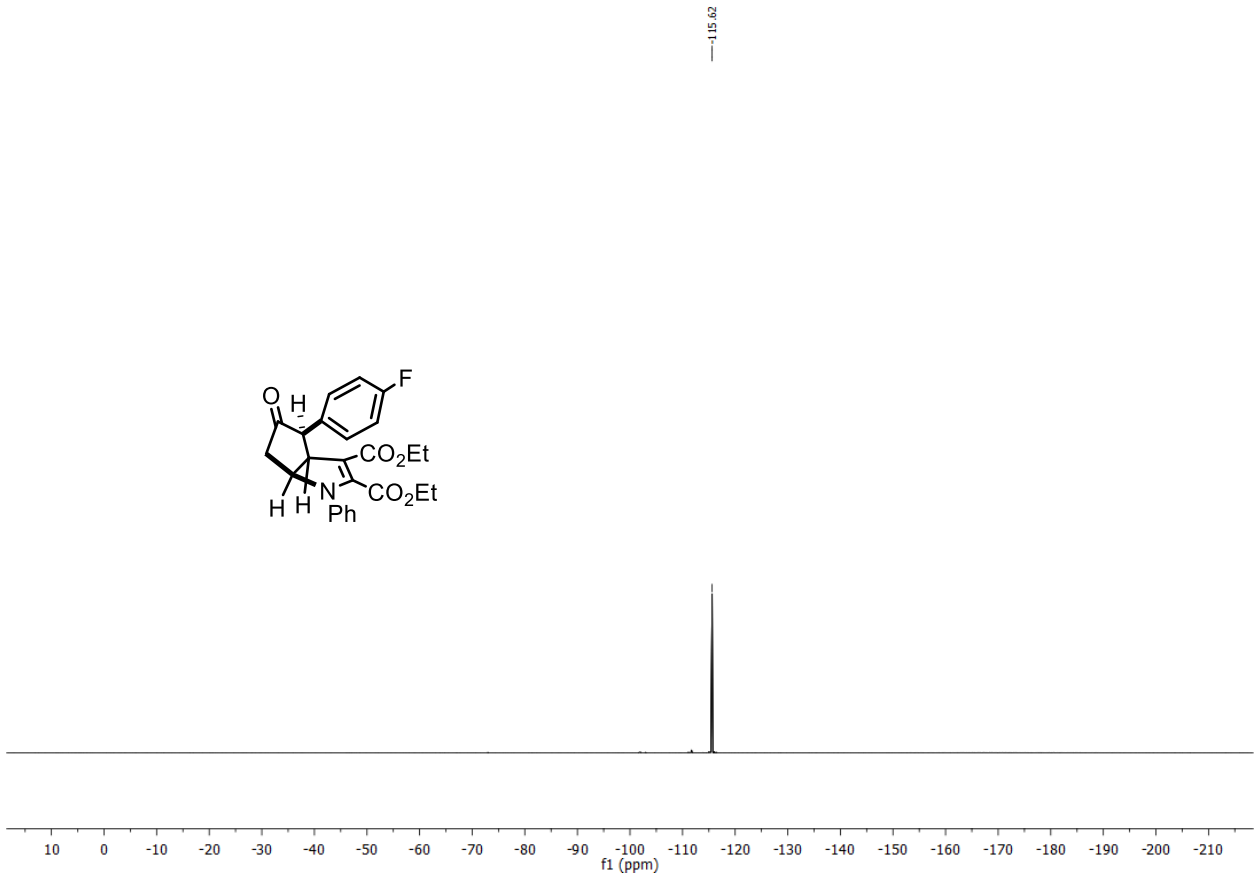




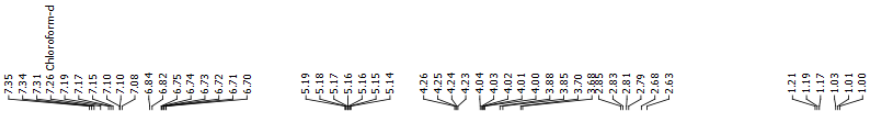


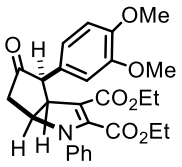


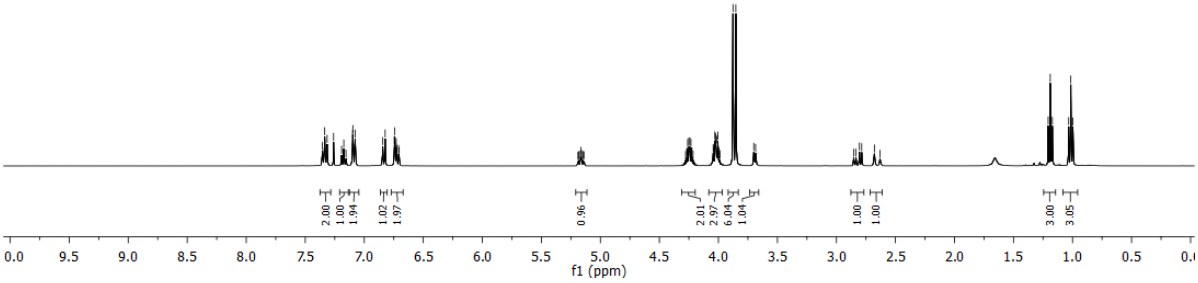
*^{19}F-NMR spectra at 400MHz **(30)***

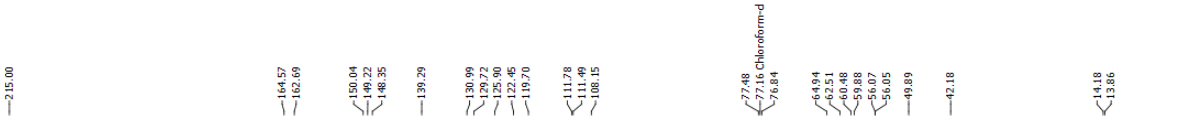


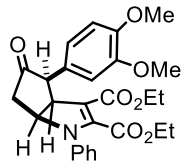
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(31)***

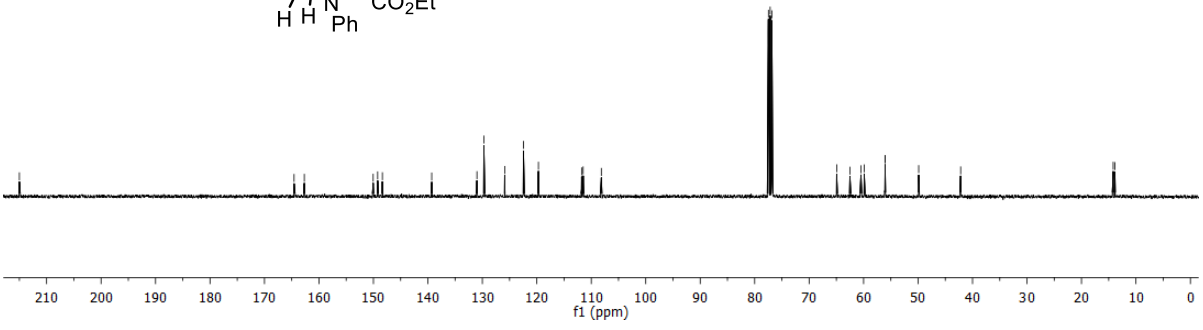




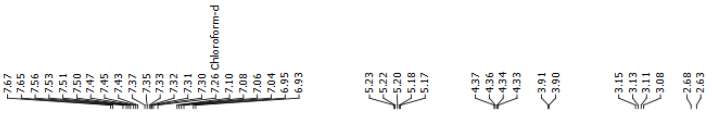


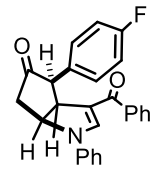


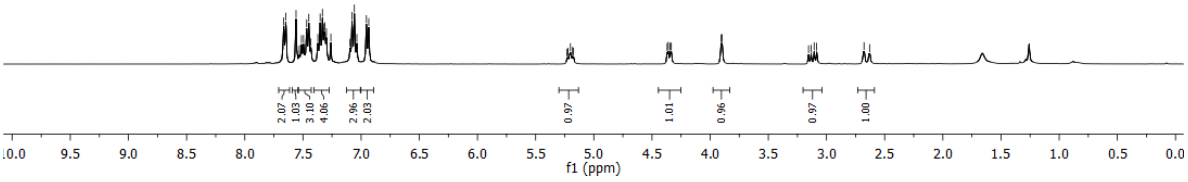


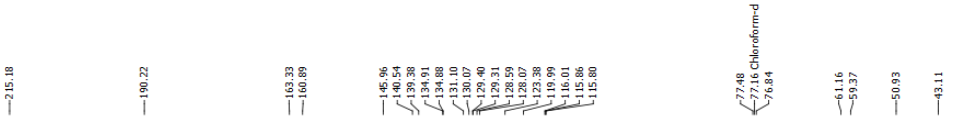


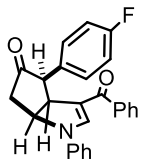
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(32)***



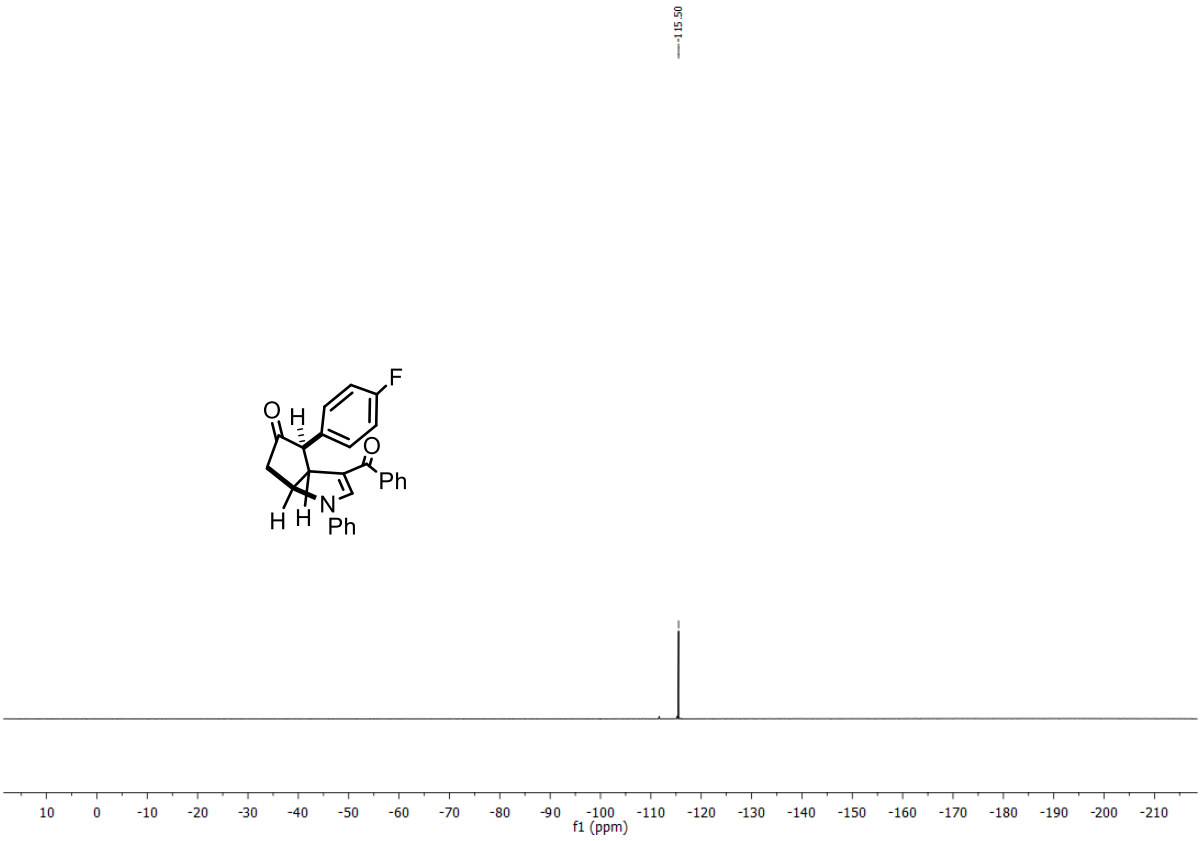




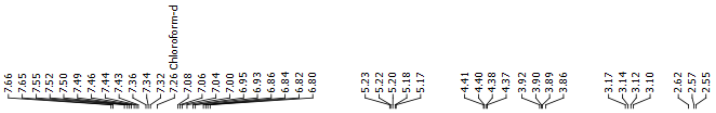


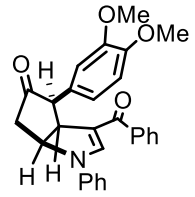


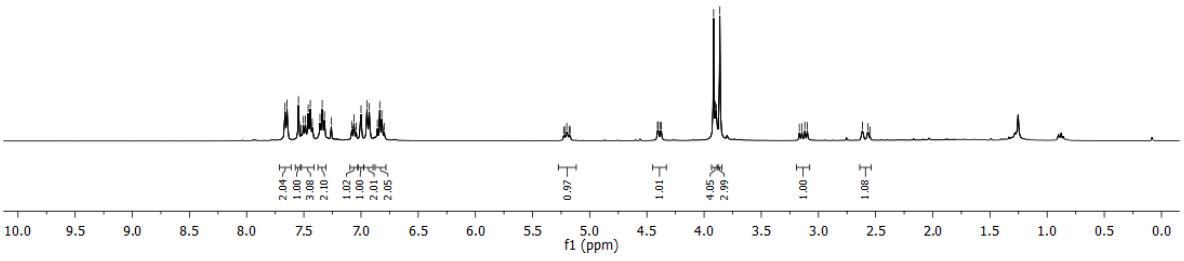
*^{19}F-NMR spectra at 400MHz **(32)***

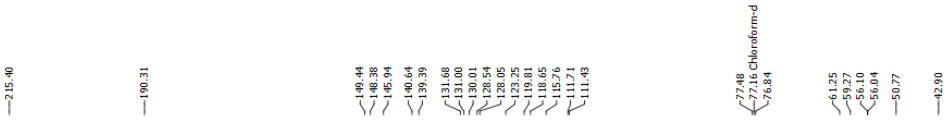


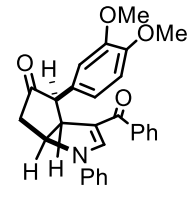
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(33)***

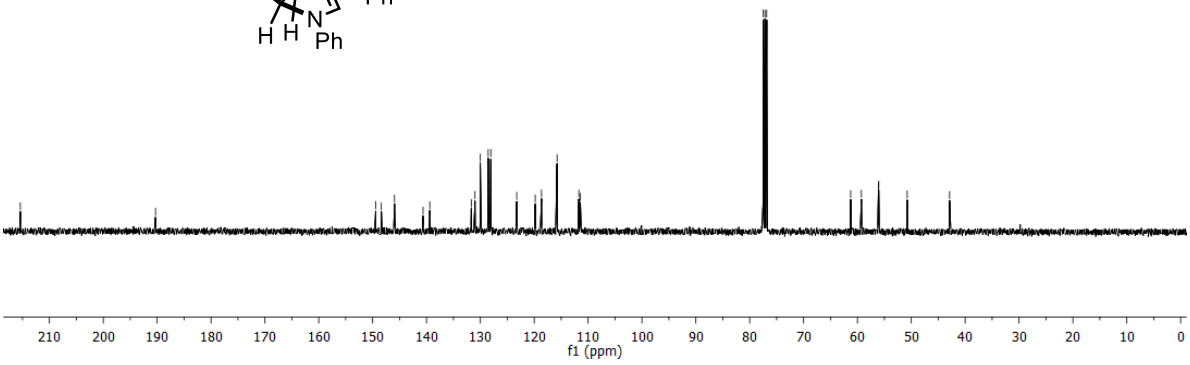




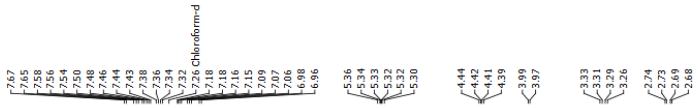


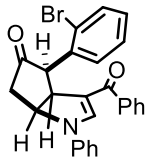


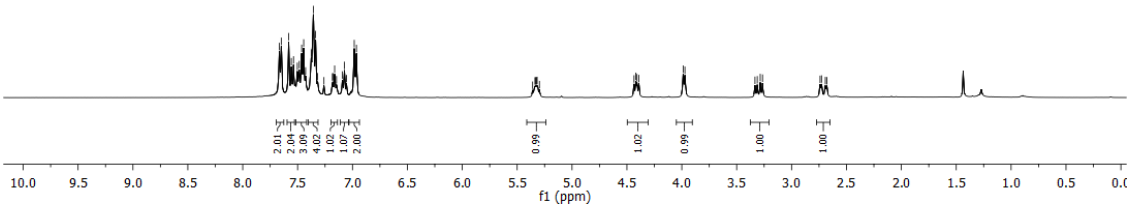


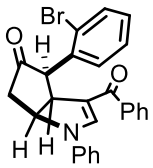


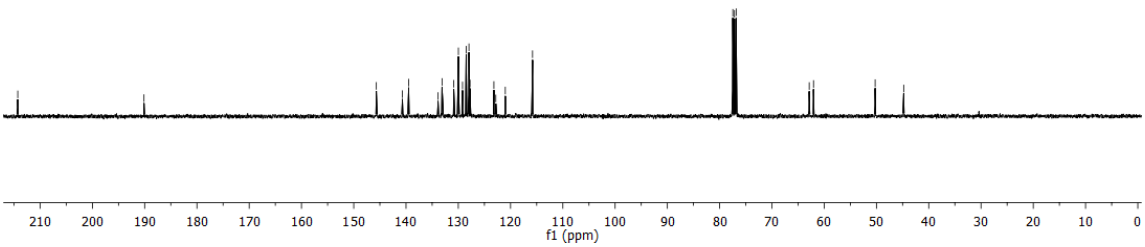
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(34)***



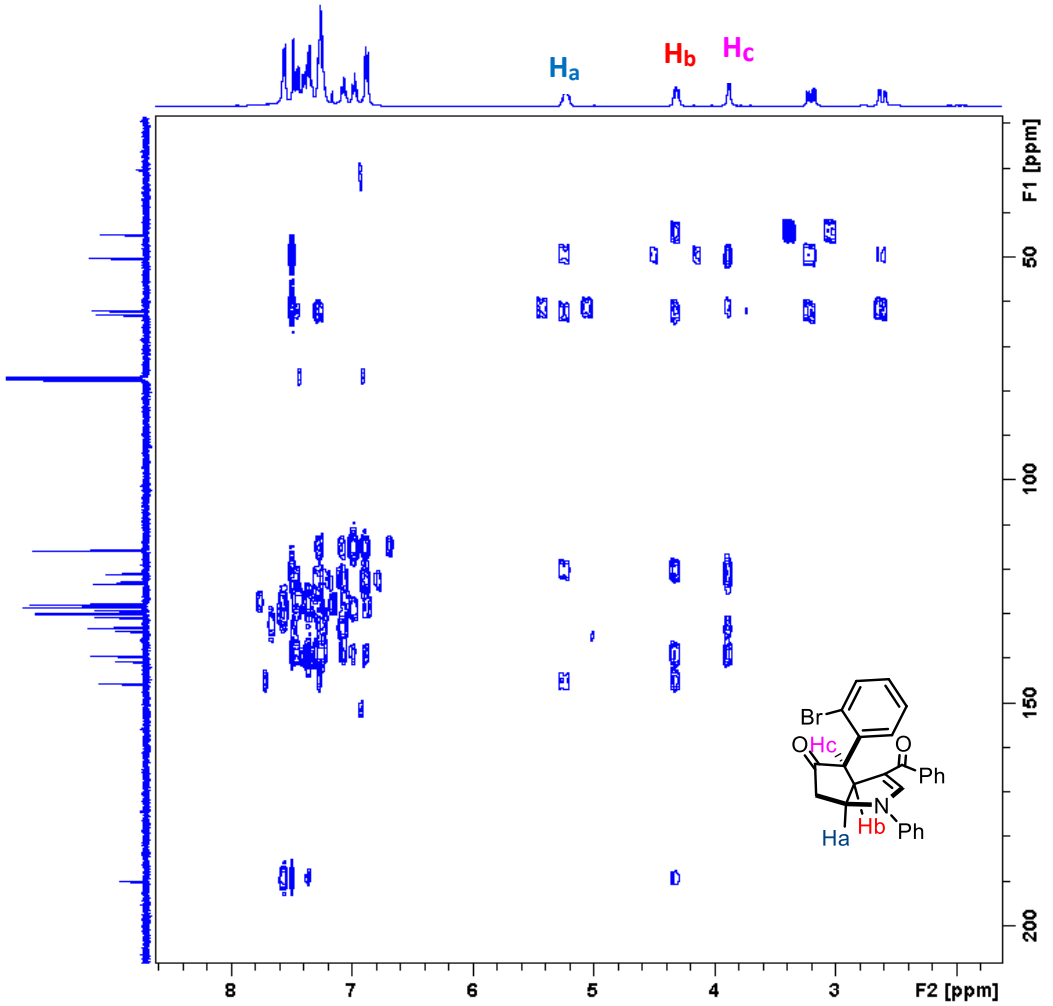




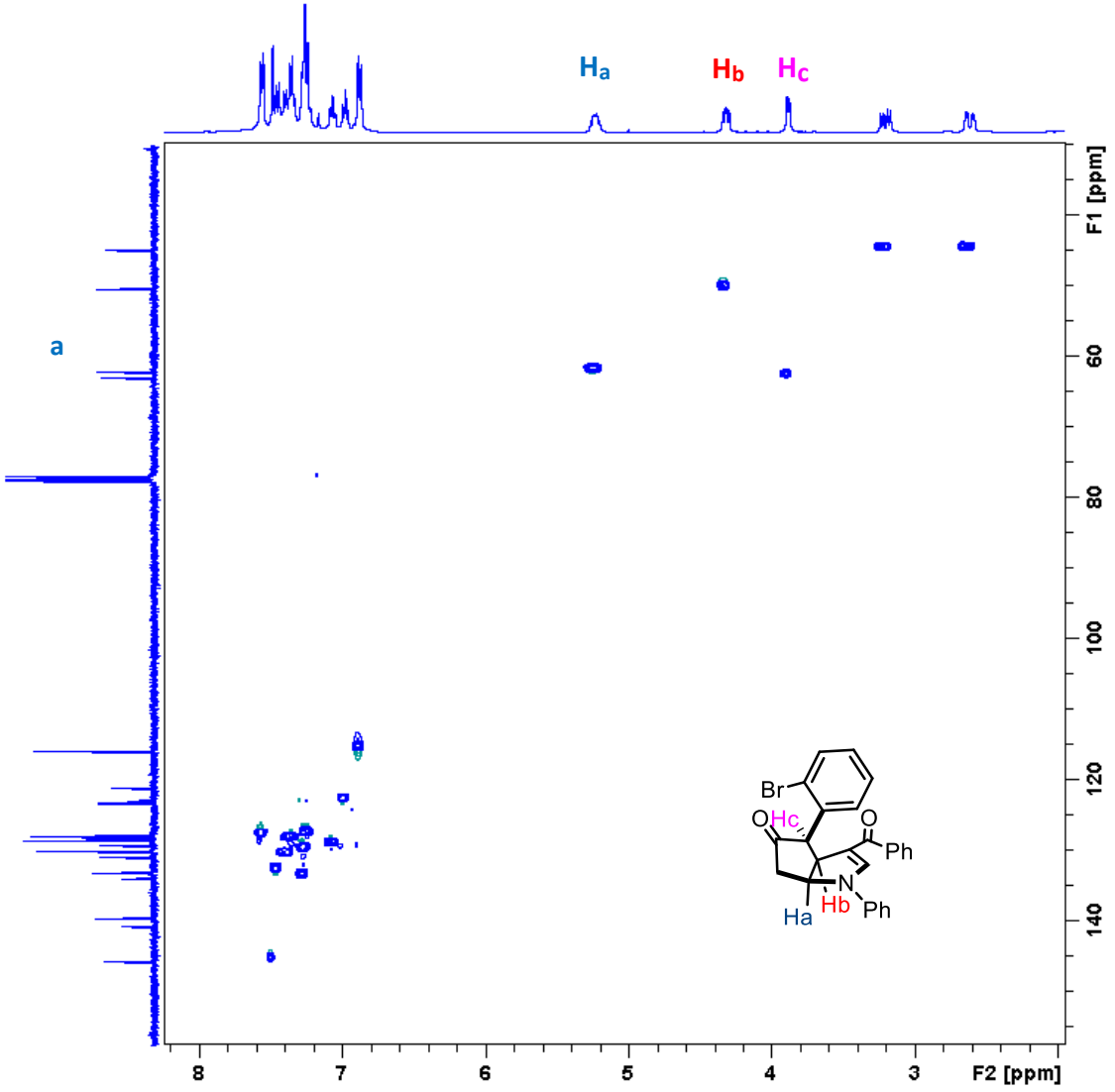




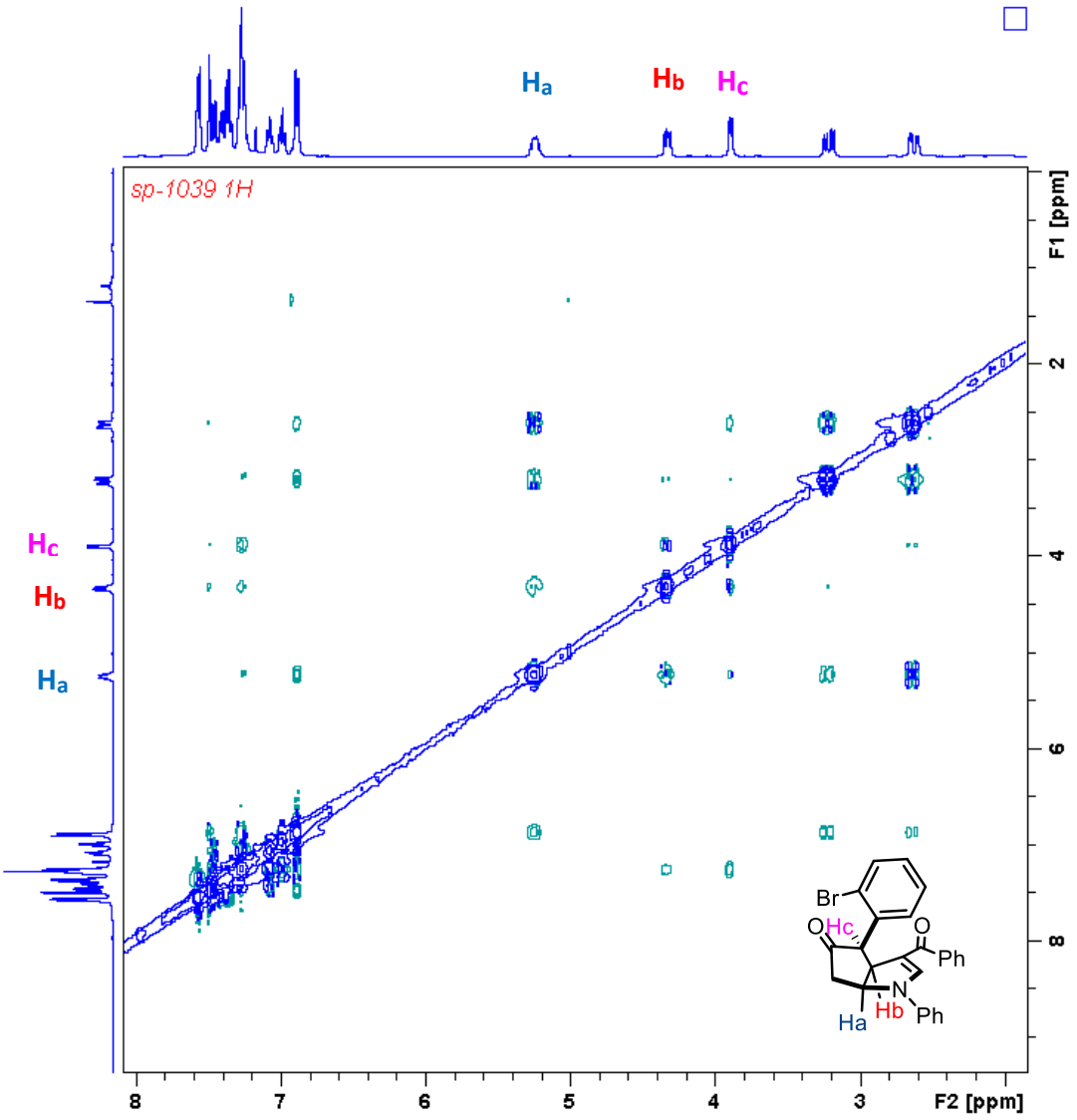
HMBC (34)



HSQC (34)


Ha
Hb
Hc
a
F1 [ppm]
60
80
100
120
140
8
7
6
5
4
3
F2 [ppm]
Br
O
Hc
O
Ph
N
Hb
Ph
Ha

NOESY (34)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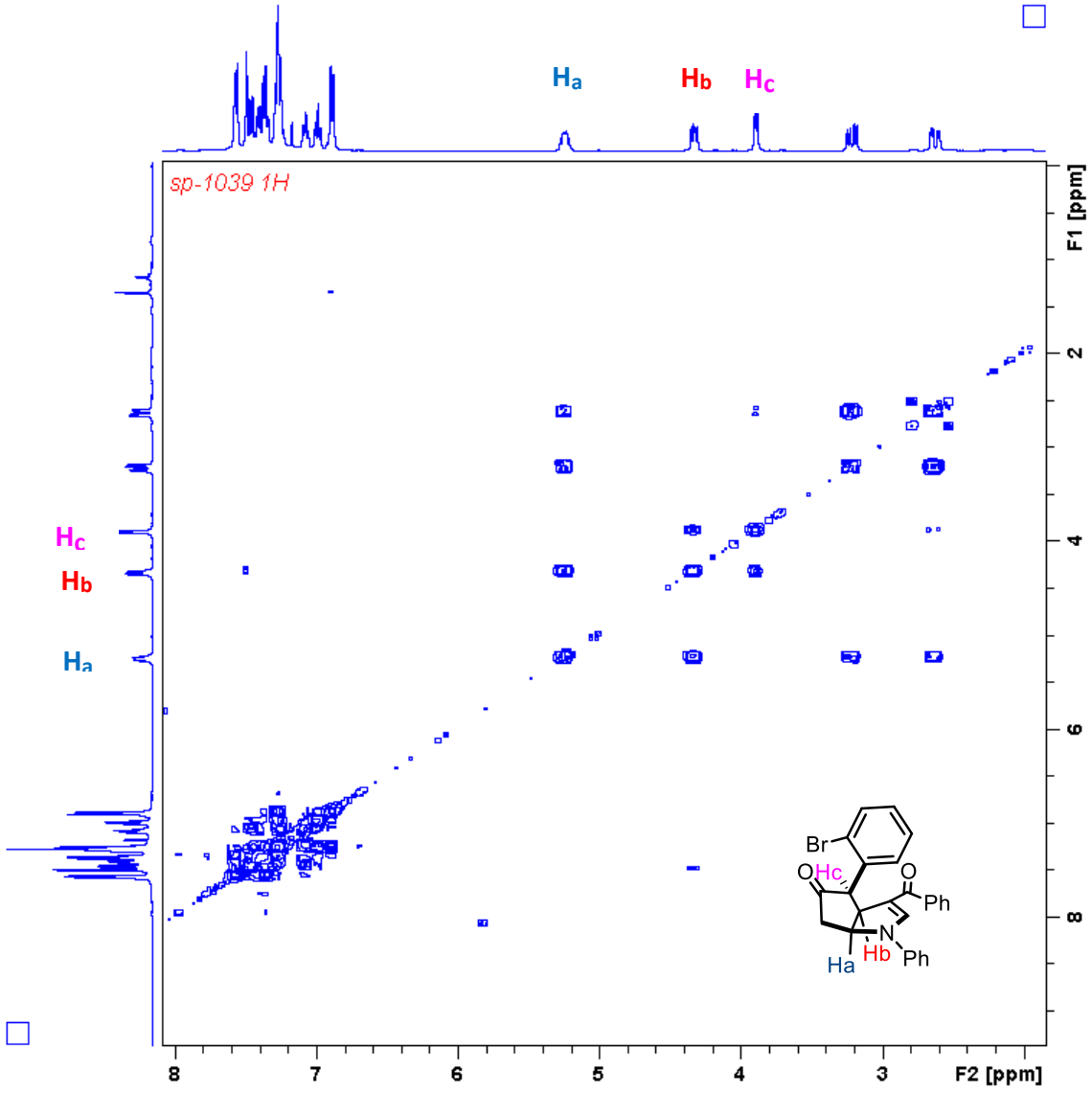
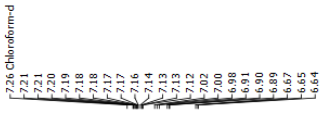
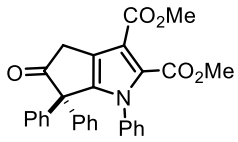
Hb
Hc
sp-1039 1H
Hc
Hb
Ha
F1 [ppm]
2
4
6
8
8
7
6
5
4
3
F2 [ppm]
Br
O
Hc
O
Ph
N
Hb
Ph
Ha

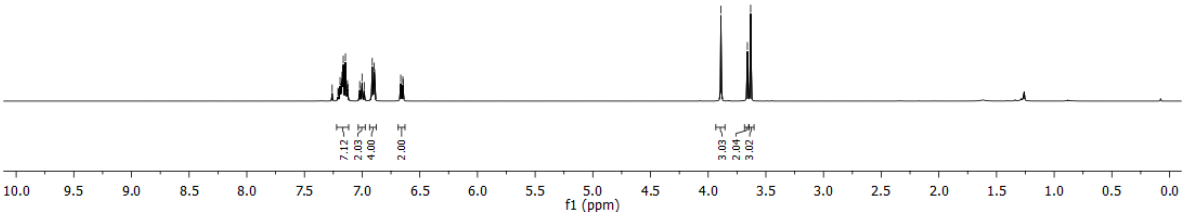
COSY (34)

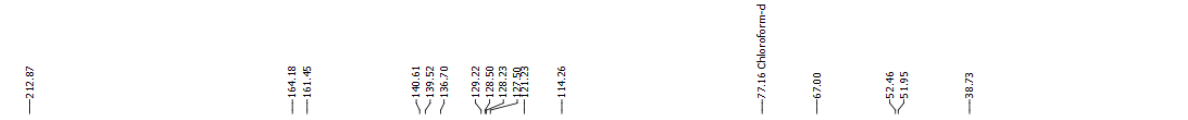

Ha
Hb
Hc
sp-1039 1H
Hc
Hb
Ha
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3
2
4
6
8
Br
O
Hc
O
Ph
N
Ha
Hb
Ph

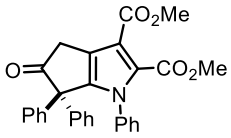
*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(35)***

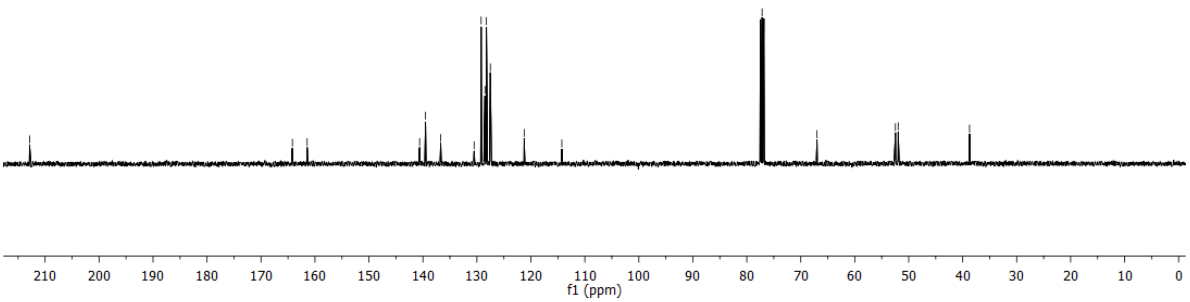




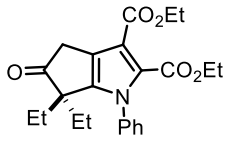


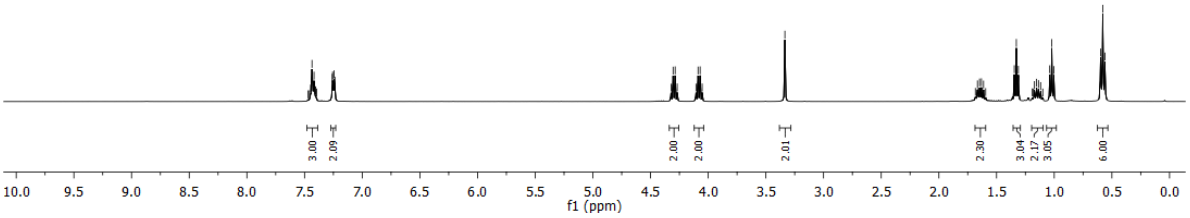


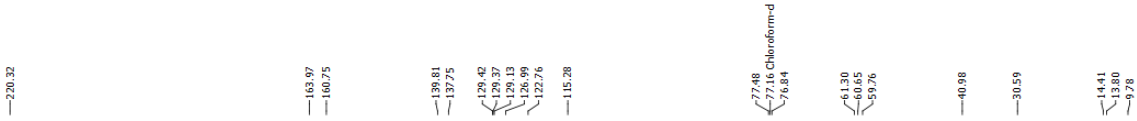


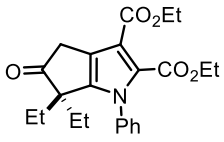


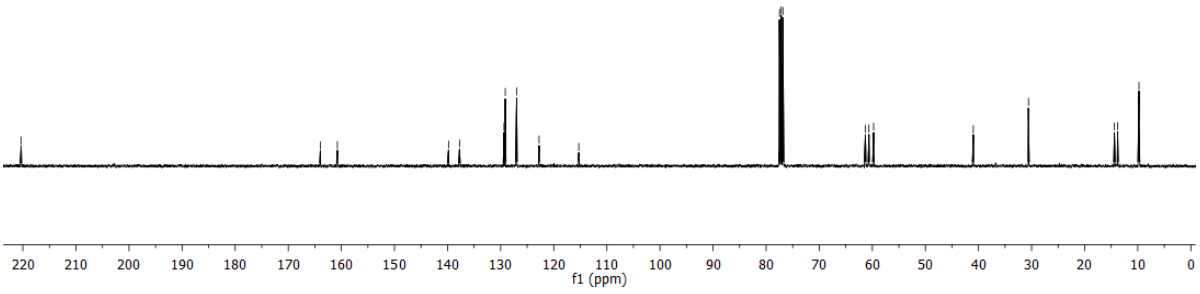
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(36)***



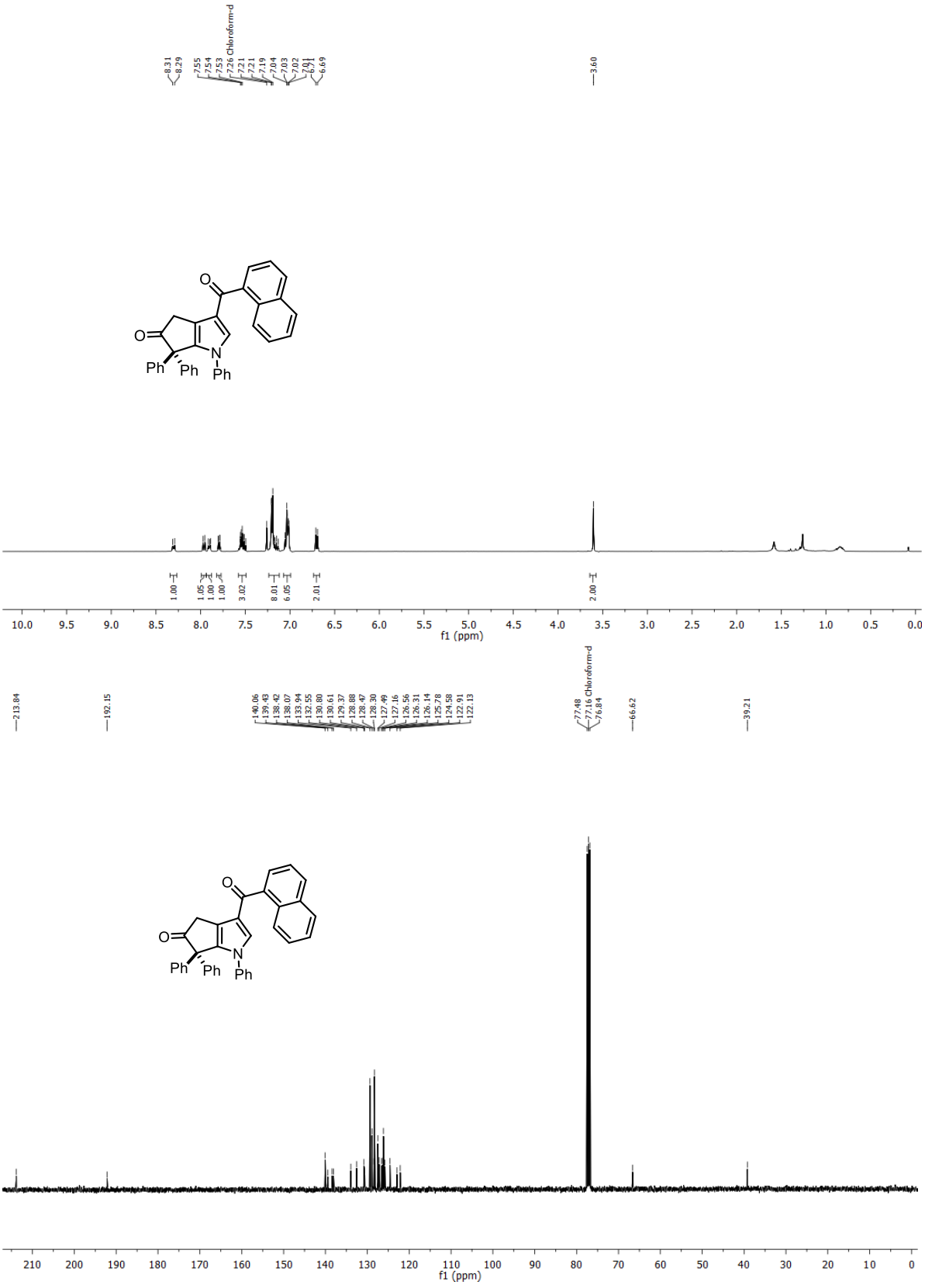




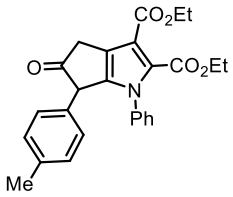


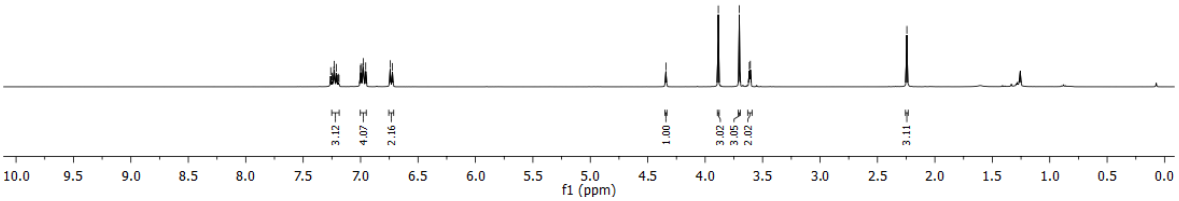


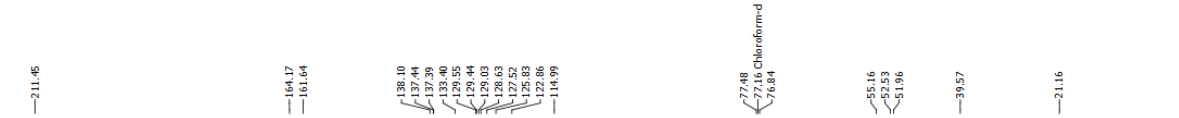
*^{1}H NMR NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(38)***

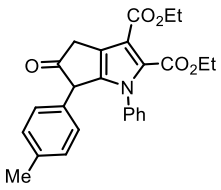


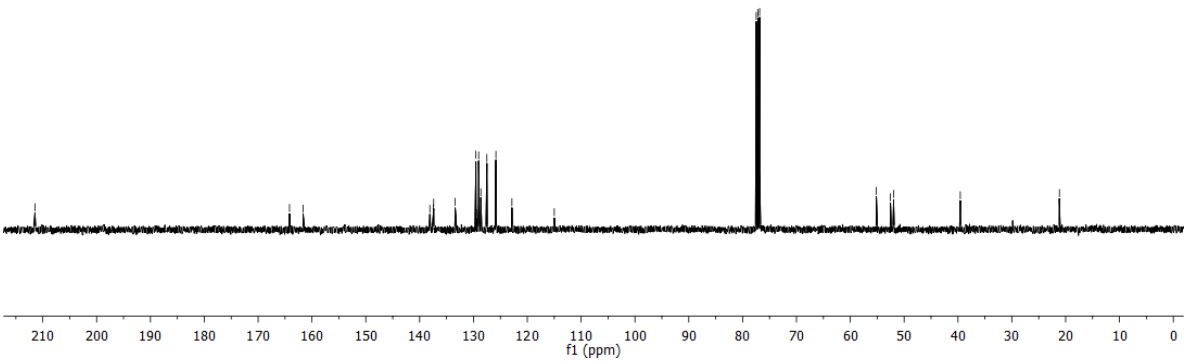
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(39)***



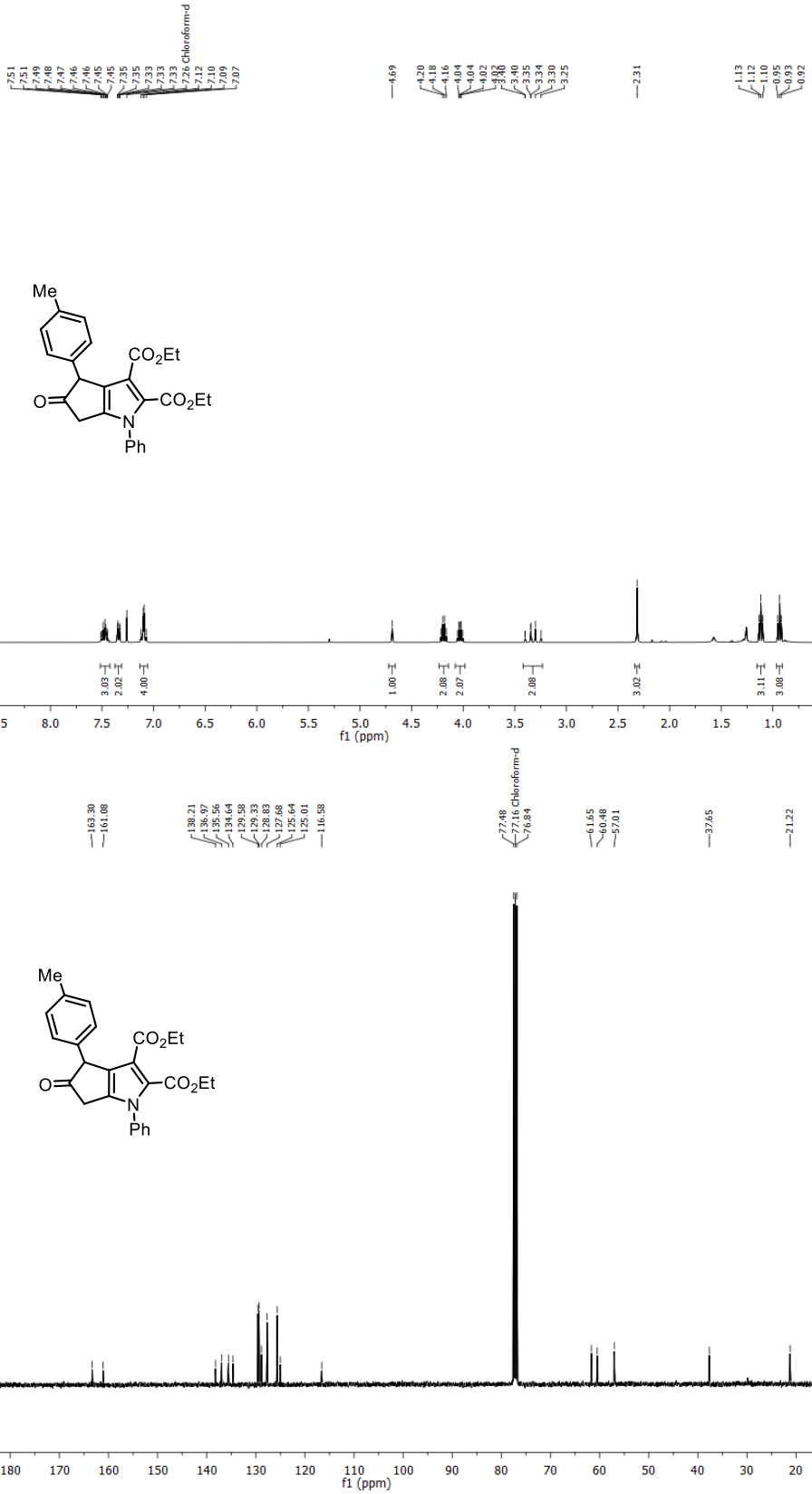




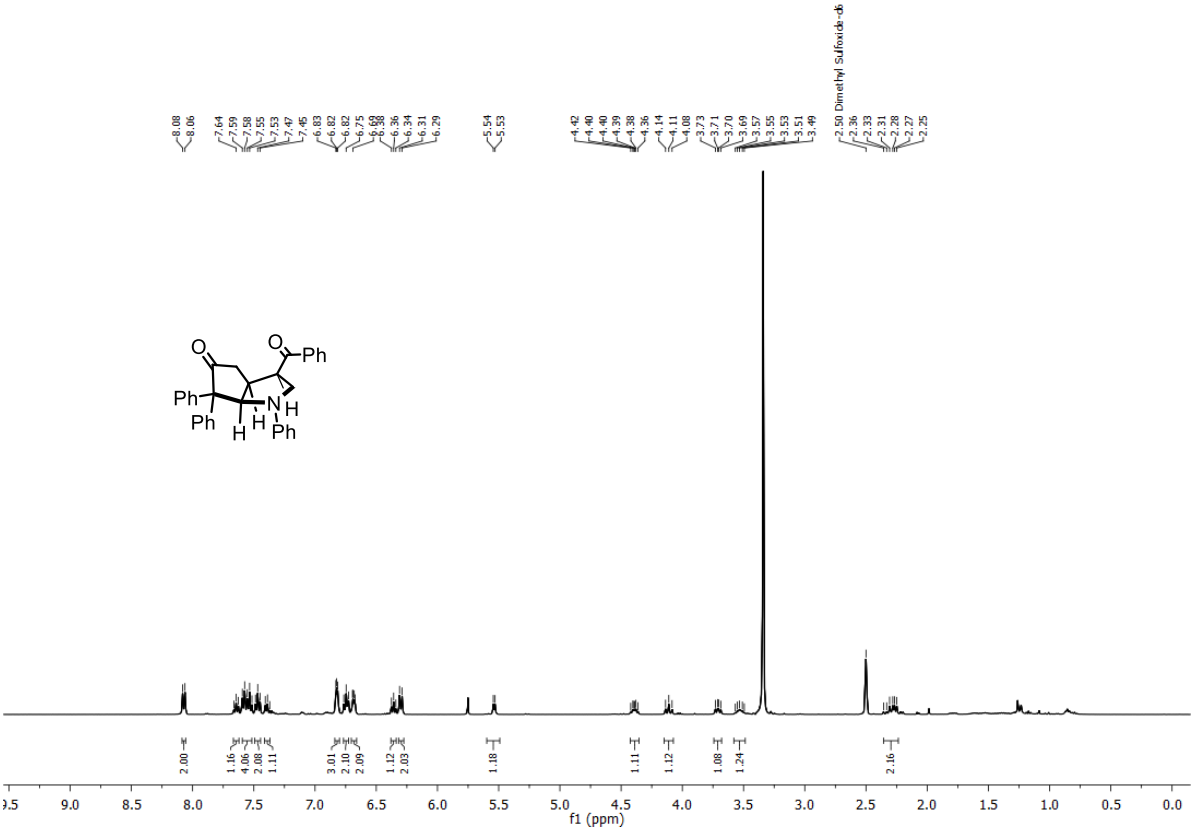


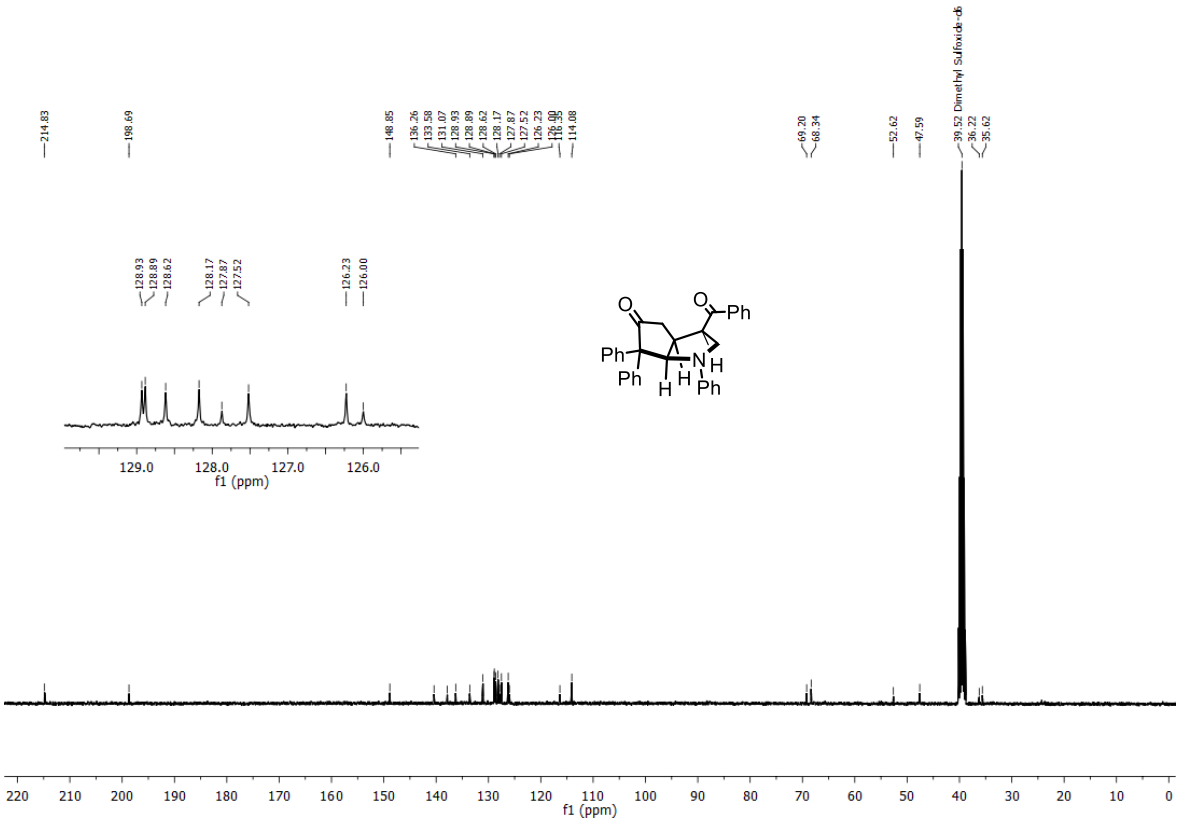


*^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$**(40)***

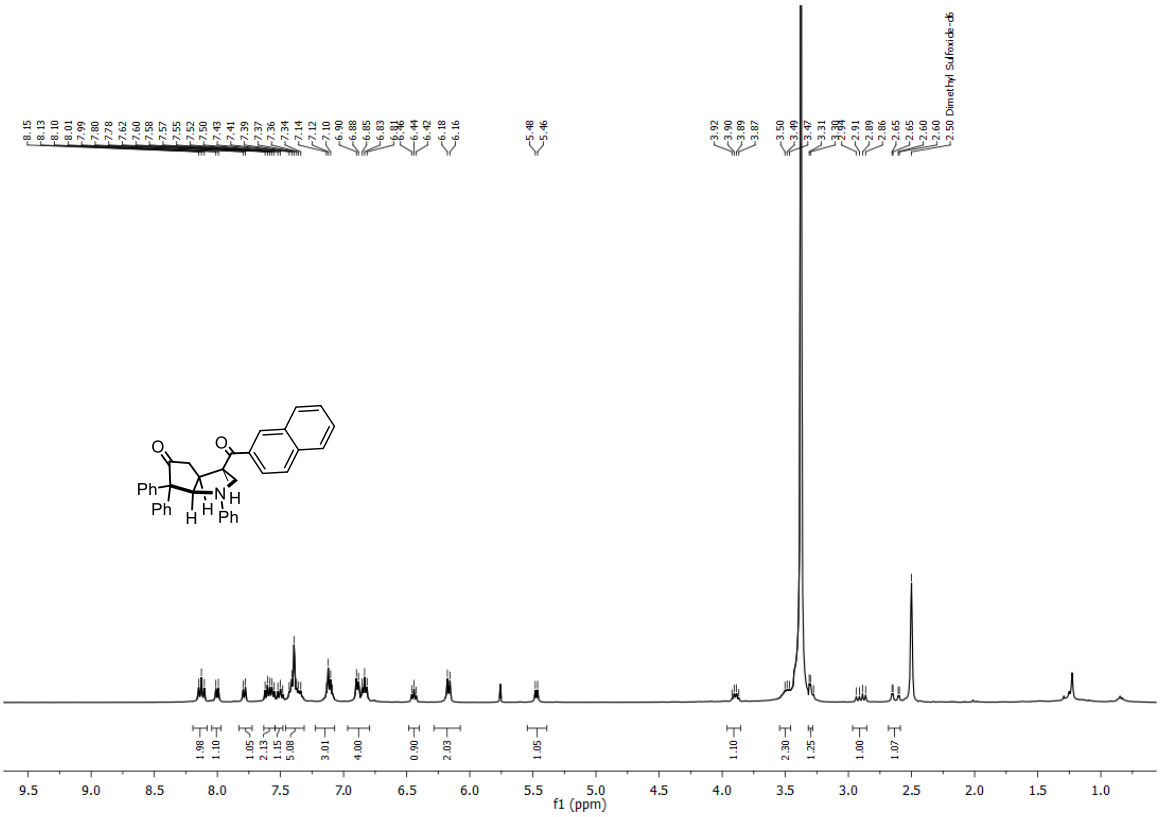


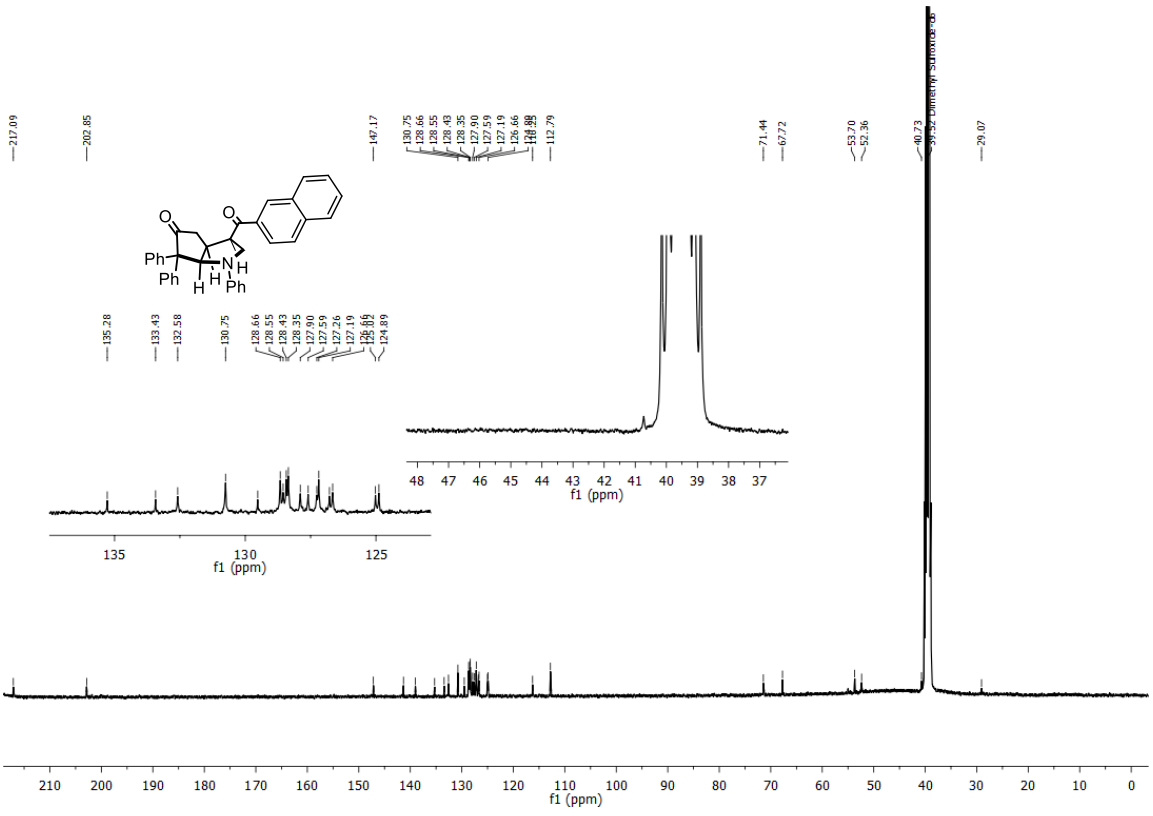
^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in DMSO ***(41)***



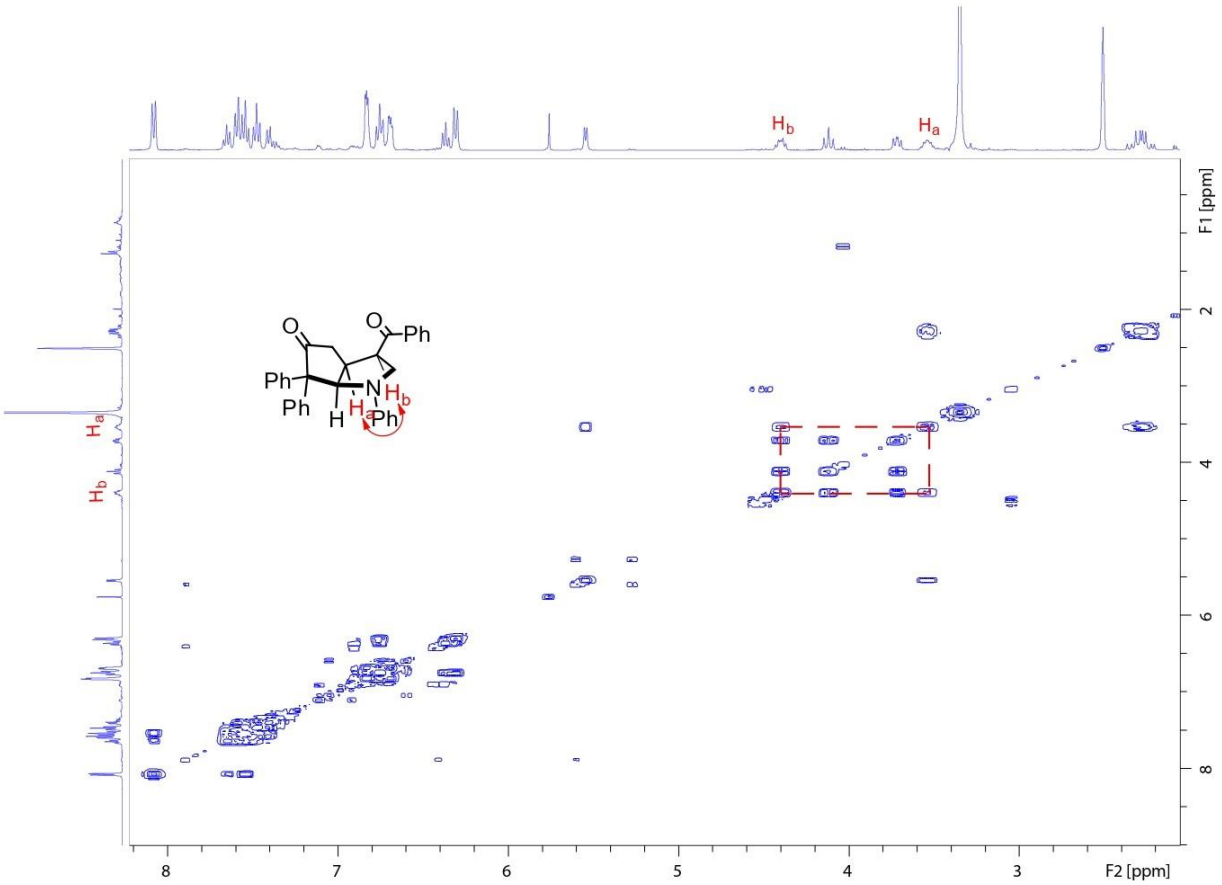


^{1}H NMR spectra at 400MHz and ^{13}C NMR spectra at 100MHz in DMSO ***(42)***

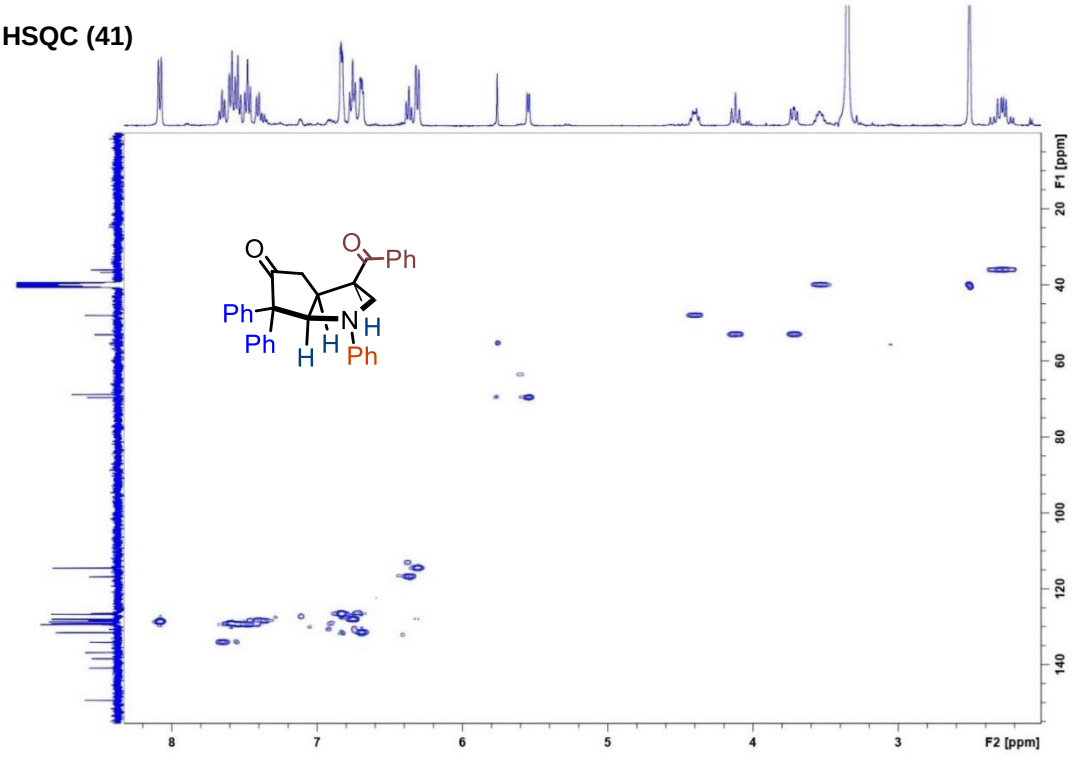




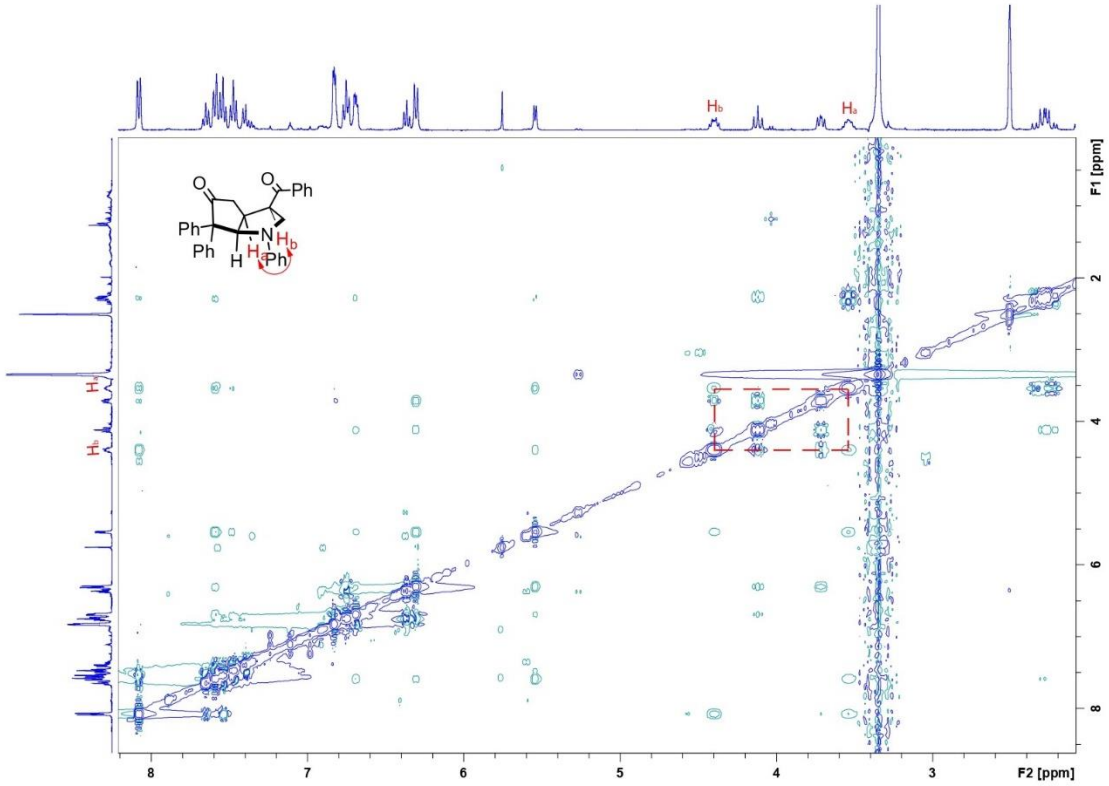
^{1}H-COSY (41)



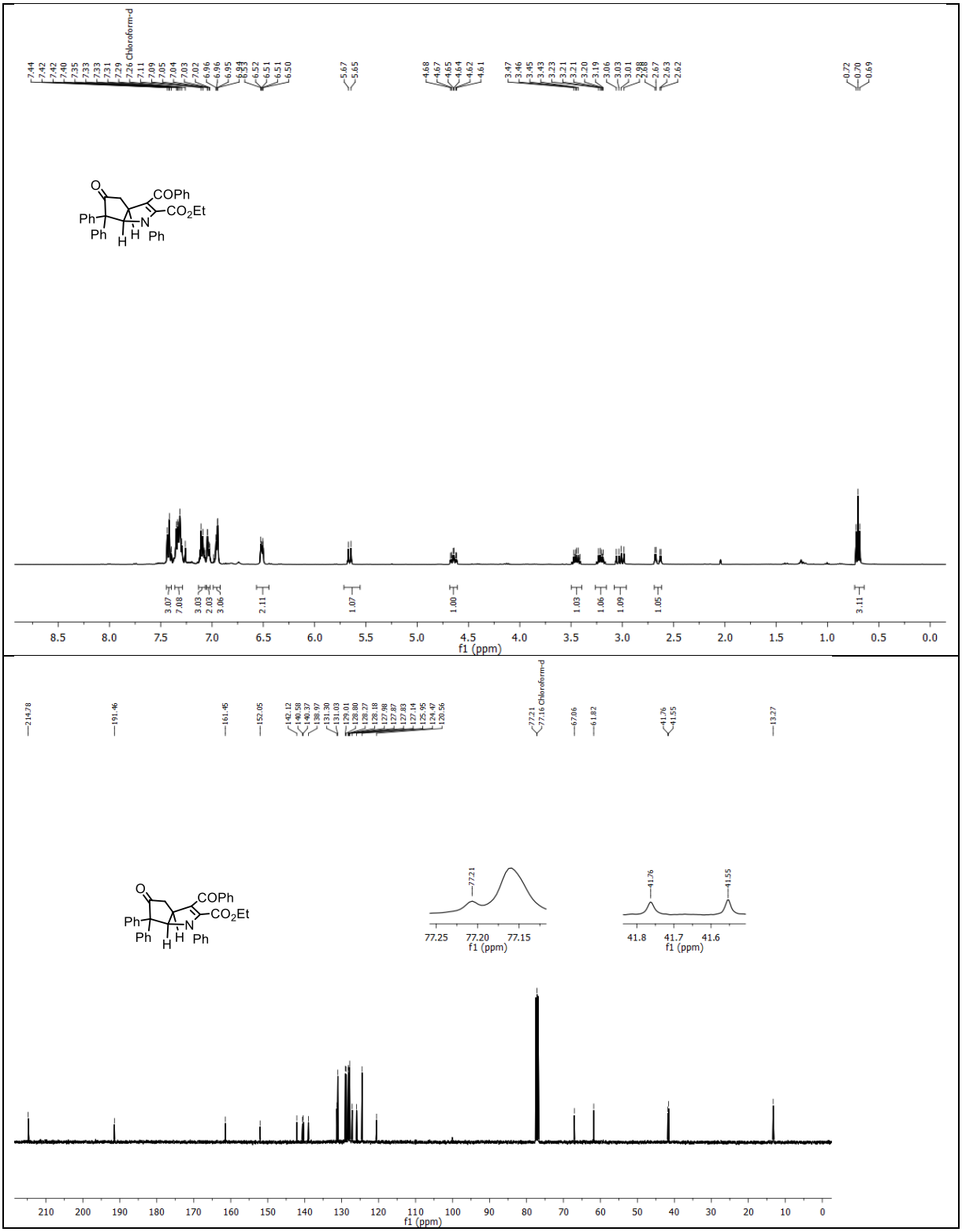
HSQC (41)



NOESY (41)



^{1}H NMR spectra at 400 MHz and ^{13}C NMR spectra at 100MHz in $CDCl_3$ ***(46)***



14. References

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